SCHOOL OF
CIVIL ENGINEERING

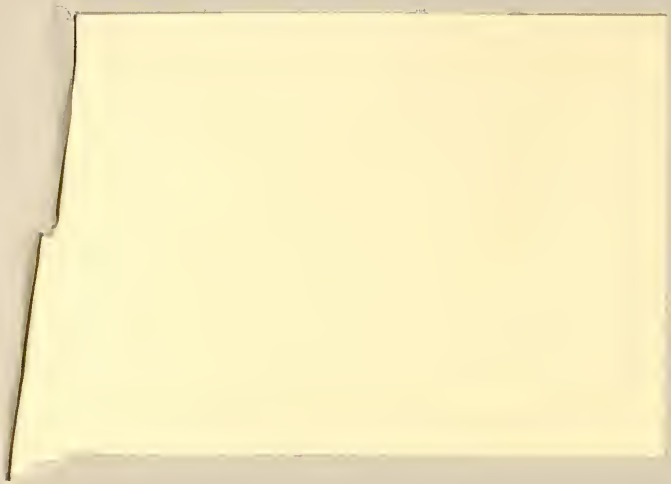
INDIANA
DEPARTMENT OF TRANSPORTATION

JOINT HIGHWAY RESEARCH PROJECT
Final Report
FHWA/IN/JHRP-90/9

THE EFFECTS OF BAG HOUSE FINES AND INCOMPLETE COMBUSTION PRODUCTS IN A DRUM DRIER ON THE CHARACTERISTICS OF ASPHALT PAVING MIXTURES - PHASE I

T. B. Nelson
L. E. Wood

PURDUE UNIVERSITY



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Final Report

The Effects of Bag House Fines and Incomplete Combustion Products in a Drum Drier on the Characteristics of Asphalt Paving Mixtures - Phase I

To: Harold L. Michael
Joint Highway Research Project

August 22, 1990

Project: C-36-6II

From: Leonard E. Wood
Research Engineer

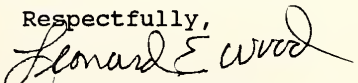
File: 2-4-35

This letter will serve to transmit the final report titled "The Effects of Bag House Fines and Incomplete Combustion Products in a Drum Drier on the Characteristics of Asphalt Paving Mixtures - Phase I". It was prepared by T. Nelson and L. E. Wood and represents the work of T. Nelson of our staff.

This report concentrates on the aspects of incomplete combustion products in asphalt paving mixtures and contains 10 chapters. Chapter 2 is a literature review that covers the pertinent information on asphalt composition and the use of high pressure gel permeation chromatography. Chapter 3 describes the equipment and materials used in this study. Chapter 4 presents the outline of the experiment. The results of the tests on the original asphalts, the tests on the aging of asphalts, and the tests for fuel contamination are given in Chapter 5, 6, and 7. A discussion of test results is covered in Chapter 8. The summary and conclusions for the project are outlined in Chapter 9. Chapter 10 presents some recommendations for further study.

This report is presented for review and approval as evidence of fulfillment of the objectives of this project.

Respectfully,



Leonard E. Wood
Research Engineer

LEW:cr

cc:
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J. D. Fricker
D. W. Halpin
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T. D. White

Final Report

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by

T. B. Nelson
and
L. E. Wood

Joint Highway Research Project

Project No.: C-36-6II
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16. Abstract

The major purpose of this study was to use the high pressure-gel permeation techniques to evaluate the changes in asphalt subjected to different mix production parameters, including plant type, level of aging and fuel used in the burner of the drier. Additional objectives were to establish correlations between physical parameters of asphalts and their chromatographic parameters, and to determine whether the HPGPC technique could be used to detect burner fuel contamination in the mix produced by asphalt plants.

This study determined that the HPGPC technique is an excellent comparative analysis tool, capable of detecting changes in the aging of asphalt, but not repeatably capable of establishing direct relationships between chromatograms and physical parameters. Results of the study also show that no significant differences could be found by HPGPC between mixes produced by drum plants and batch plants, or by plants using different burner fuels. HPGPC can also detect fuel contamination at the 1% contamination level, not detectable by physical measures. Finally, results of this study show that the 5 hour thin film oven test does not simulate aging produced by asphalt plants, and should be reevaluated.

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ABSTRACT

The widespread adoption of the drum mix asphalt plant and the operating parameters associated with this plant has resulted in increased speculation as to the characteristics of the asphaltic concrete mix produced when compared with batch plant mixes. The use of lower grade burner fuels in both plants to dry the aggregate has furthered this concern. These concerns have recently reached a peak with reports of premature pavement failures due to these or other causes.

An evaluation of these problems may be aided by the use of high pressure-gel permeation chromatography (HPGPC). This technique has recently been utilized by some researchers to study and characterize asphalts. The major purpose of this study was to use this technique to evaluate the changes in asphalt subjected to different mix production parameters, including plant type, level of aging and fuel used in the burner of the drier. Additional objectives were to establish correlations between physical parameters of asphalts and their chromatographic parameters, and to determine whether the HPGPC technique could be used to detect burner fuel contamination in the mix produced by asphalt plants.

Samples of asphalt cement, asphaltic concrete mix produced with these samples, and the burner fuels used to

produce them were collected during the 1985 paving season. These samples, along with pavement cores taken after five years of service life were analyzed by physical and chromatographic techniques. Additionally, samples were artificially contaminated with burner fuels and evaluated.

This study determined that the HPGPC technique is an excellent comparative analysis tool, capable of detecting changes in the aging of asphalt, but not repeatably capable of establishing direct relationships between chromatograms and physical parameters. Results of the study also show that no significant differences could be found by HPGPC between mixes produced by drum plants and batch plants, or by plants using different burner fuels. HPGPC can also detect fuel contamination at the 1% contamination level, not detectable by physical measures. Finally, results of this study show that the 5 hour thin film oven test does not simulate aging produced by asphalt plants, and should be reevaluated.

CHAPTER 1

INTRODUCTION

1.1 - Background

Major changes have occurred in the production of hot mix asphaltic concrete over the past fifteen years. Collectively, these changes have led to uncertainties when attempting to identify specific causes of asphalt pavement distress. As these distresses have increased in frequency and severity, efforts have been made to characterize the changes in the original asphalt, the production process, and the resulting mixes.

One of the major changes in the production of hot mix asphaltic concrete has been the introduction of the drum mix asphalt plant. The economic savings associated with this system has led to its widespread adoption within the paving industry. Today drum mixers comprise over 90% of new asphalt plant sales.

In 1973, shortly following the introduction of the drum mix process to the industry, an oil embargo further complicated the asphalt production process. This embargo created a disruption in the supply of crude normally received by refineries, and led to changes in the processing of the crudes. This resulted in asphalts

leaving the refineries with characteristics that were different than previously measured. In order to decrease the differences found in these asphalts, and to minimize disruption possibilities, crudes were often blended before being shipped to a geographic area.

Higher energy costs attributed to the oil embargo also led to the use of alternative sources of fuel for heating and drying aggregates in asphalt plants. Reclaimed oils and fuel oils of lower grade were often utilized. These fuels, along with the drum mix technology, resulted in different combustion characteristics than gas and light fuel oils in conventional batch plants. Incomplete combustion could result from improper burner settings and plant operation. Incomplete fuel combustion could produce products that potentially effect asphalt properties. This effect on the asphalt compounds the changes being experienced from changing crude sources and asphalt production.

The resulting changes in asphalt characteristics have been blamed for the pavement distresses that have been occurring. In Indiana, some asphalt overlays have been observed to exhibit premature rutting or flushing with a subsequent loss of friction. In some cases these distresses have required replacement of mixes in a matter of months. Unless problems of this type can be solved, paving costs will escalate to an unacceptable level. Identification of problems in the asphalt mix production

process and changes in the characteristics of both the original asphalt and the resulting mix will help reduce the early appearance of these distresses. The paving industry could avoid poorly performing asphalts or design for the characteristics of the hot asphalt mix that is being produced by the particular asphalt mix production process.

1.2 - Purpose and Scope

The initial goal of this study was to determine whether the incomplete combusion of fuels in drum mix plants could be detected from chromatographic analysis of extracted asphalt. In order to perform this study it was necessary to develop high pressure-gel permeation chromatography (HPGPC) techniques. As part of developing the HPGPC procedures, asphalt samples were contaminated in the laboratory with various fuels. Chromatograms and asphalt properties of these laboratory samples were compared to determine contamination detection.

A second goal of this study was to use HPGPC techniques to analyze asphalts from sources and pavements in Indiana to build a data base of chromatograms. These chromatograms can be used to examine differences in asphalts from various sources, changes in asphalt from different mix production processes, and changes with time from in-service pavements. The asphalts and pavement mix samples used to develop this baseline data base were obtained during the 1985 construction season. Cores from these in-service pavements were taken in

1990, and the asphalt extracted. The extracted asphalt was compared to chromatograms of the original asphalt and asphalt extracted from the original paving mixtures to provide a basis for evaluating in-service aging.

A third goal of the study was to evaluate how the chromatograms of asphalt from different mix production processes change. This evaluation considered different types of plants, different burner fuels, and the effects of aging through time. The data base of chromatographic information from this study could be used by the Indiana Department of Transportation (INDOT) for future evaluation of asphalts at various stages of processing and prediction of the changes in asphalt properties through this processing. These techniques can also be used to compare laboratory aging with in-service aging.

1.3 - Organization

This dissertation is organized in ten chapters. Following this introductory chapter is a chapter that reviews the literature dealing with asphalt composition and properties, the asphalt concrete mix production process, including factors which may contribute to distresses found in asphalt, and the analytical techniques used to analyze the asphalt properties. Chapter 3 describes the equipment and materials used in this study, while Chapter 4 presents a discussion of the analysis procedures. The results of HPGPC

analysis are presented in Chapters 5 through 7. Chapter 8 contains a discussion of the results. Chapter 9 presents a summary and conclusions, and Chapter 10 presents recommendations for further study.

CHAPTER 2

LITERATURE REVIEW

The first section of this chapter presents an overview of asphalts, their composition, and methods used to characterize their composition.

The second section describes high pressure-gel permeation chromatography (HPGPC) and how this technique has been utilized to evaluate asphalts. This section discusses how the HPGPC technique has been used to attempt to relate performance of asphalt mixes to the properties of the asphalt. The effects of asphalt mix production techniques on the properties of asphalt is discussed in the third section. This discussion includes the two distinct types of asphalt plants, drum mix and batch plants, and their resulting mixes. The final section discusses some of the physical measures of asphalt properties and performance and how they relate to asphalt composition.

2.1 - Asphalt Composition and Characterization

2.1.1 - Asphalt Composition

Asphalt is defined by ASTM as "a dark brown to black cementitious material in which the predominating constituents are bitumens which occur in nature or are

obtained in petroleum processing" [1]. The naturally occurring bitumens, such as those found in Trinidad Lake, were extensively used for ship caulking, adhesives and waterproofing during Columbus' time, and have been mentioned as far back in history as biblical times [2]. With the first use of asphalt for road paving in London, England in 1869, and in Newark, New Jersey a year later, demand for asphalt increased; a demand that led to development of the production of asphalt cements from crude petroleum.

Whether naturally occurring or processed, asphalts are composed primarily of hydrocarbons of high molecular weight. Although all asphalts contain approximately 85% carbon and 10% hydrogen atoms by weight, most also contain various amounts of nitrogen, sulfur, oxygen, vanadium and nickel. The percentages of each component found in a given asphalt depend on the crude source and the method of processing. Analysis of asphalts from four different sources performed by Peterson shows a variation in the fractional composition of asphalts [3]. Table 2-1 shows this variation in asphalts. Although the percentages of trace elements vary slightly from asphalt to asphalt, all asphalts analyzed contain approximately 95-97% carbon and hydrogen.

Table 2-1. Composition of Asphalts from Four Different Sources (from Peterson [3])

Element	Asphalt Source			
	I	II	III	IV
Carbon, %	83.77	85.78	82.90	86.77
Hydrogen, %	9.91	10.19	10.45	10.94
Nitrogen, %	0.28	0.26	0.78	1.10
Sulfur, %	5.25	3.41	5.43	0.99
Oxygen, %	0.77	0.36	0.29	0.20
Vanadium, ppm	180	7	1380	4
Nickel, ppm	22	0.4	109	6

In order to simplify the plethora of possible molecular structures for asphalt, estimated by Peterson [3] to be on the order of 10^{20}, three basic types of molecular structure are generally defined. The first of these is the aliphatic type, also referred to as paraffinic. This is the simplest structure, in which carbon atoms are arranged in straight or branched chains. Asphalts typically contain between 35 and 60 percent paraffinic structures.

The second type of structure is the napthenic type, which consists of saturated rings of carbon atoms. These structures have a two to one hydrogen to carbon atom ratio, and make up between 15 and 30 percent of the asphalt structure.

The third type of structure is the aromatic type, which consists of a six carbon ring with a system of one to ten rings surrounding the base ring. The aromatic carbon structure accounts for 25 to 35 percent of asphalt structure. The aromatic structures also typically have other hydrocarbon chains attached to the ring systems, as do the naphtenic structures.

Aromatic ring systems or the so-called heteroatoms of sulfur, oxygen and nitrogen in the molecular structure cause polarity in the asphalt molecules. These polar molecules have an attraction for each other and form groups of associated molecules. It is the association of these attracted polar molecules that is responsible for defining physical properties such as boiling point and viscosity.

Additionally, the polar molecules can interact with aggregate and other asphalt molecules.

Due to the previously discussed number of structural variations and the reactivity of polar molecules, asphalt molecules are not separated and identified on an individual molecule basis. Rather, asphalts are typically grouped into classes of molecular types or fractions based upon their chemical functionality. This classification has been used to investigate how the different molecular types affect the chemical and physical properties of asphalts consisting of different amounts of these structures.

2.1.2 - Compositional Characterization Methods

In the separation or fractionation of asphalt into less complex generic fractions, four general processes are used. These processes include solvent fractionation, selective chemical precipitation, adsorption-desorption and chromatography.

Solvent fractionation, also termed partitioning with partial solvents, is a method attributed to Schweyer and Traxler [4]. Shown schematically in Figure 2-1, this procedure uses n-Butonal to precipitate the asphaltic fraction. The remaining solution is dissolved in acetone and chilled to precipitate the paraffins. The solution that remains is referred to as cyclics. This method, although advantageous in not altering components, is not widely used because the fractions obtained are not as distinctively different as those obtained by other methods.

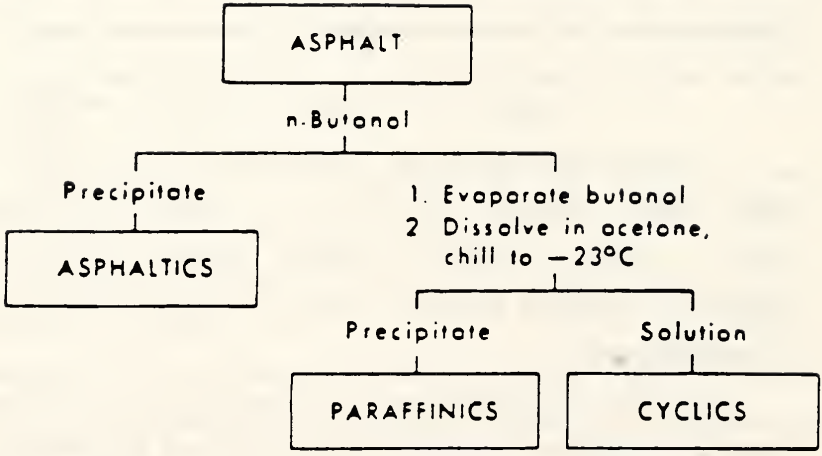

Figure 2-1. Solvent Fractionation [4]

Chemical precipitation, as developed by Rostler and Sternberg [5], is depicted in Figure 2-2. An n-pentane solvent is used first to separate the asphaltene fraction. The remaining solution is separated into three maltene fractions by using different concentrations of sulfuric acid. These three fractions are the nitrogen bases, 1st acidaffins, and 2d acidaffins. The remaining solution is referred to as the paraffins, and constitute the oily component of asphalt. It is important to note that some of the steps in this process are destructive, and the method does not recover the altered fractions for further analysis.

Selective adsorption-desorption is probably the most widely used separation technique in research. Two methods are considered when discussing this technique. These methods are clay-gel and Corbett procedures [6]. Clay-gel separation uses n-pentane to precipitate the asphaltenes, and a selective adsorption-desorption process on clay-gel to separate the saturate, polar and aromatic fractions. The Corbett procedure, although similar in concept, uses n-heptane to separate the asphaltenes, and an alumina-gel to separate the maltene fractions into saturates, napthene aromatics and polar aromatics. These procedures are shown schematically in Figure 2-3.

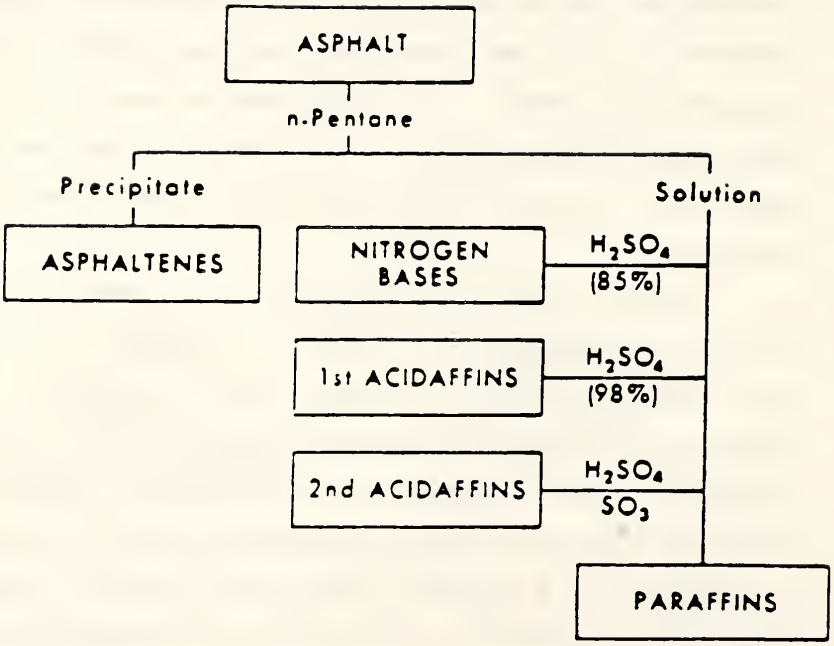

Figure 2-2. Rostler & Sternberg Procedures [5]

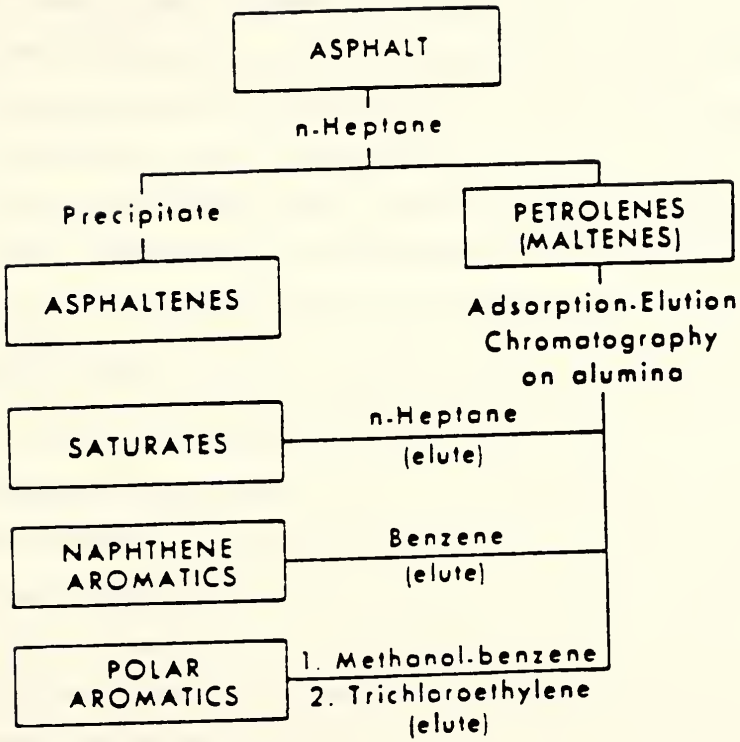

Figure 2-3. Adsorption-Desorption Technique [6]

The fourth method of separation is size exclusion chromatography, or high pressure gel permeation chromatography (HPGPC). This technique, as opposed to the previously described techniques, does not separate fractions on the basis of chemical properties, but separates fractions by molecular size. Based upon the time at which they elute, or emerge, from gel columns, asphalt molecules can be characterized very generally as asphaltenes, resins, or oils. This technique is used for the analysis of the asphalts in this study, and is discussed in more detail in the next section.

2.2 - High Pressure Gel Permeation Chromatography (HPGPC)

2.2.1 - Theory of HPGPC

The forerunner to high pressure-gel permeation chromatography is liquid chromatography. Although there are several techniques applied to chromatography, all are based upon the same principle. The material to be separated into fractions is dissolved in a solvent (mobile phase) and pumped through an adsorbent (stationary phase) column. The compounds dissolved in the mobile phase will adsorb to the stationary phase to differing extents, and will emerge (elute) from the column at different rates. A detector utilizing refractive index or ultraviolet techniques then measures the amount of separation of the fractions by "counting" the number of molecules passing the detector.

An improvement to liquid chromatography is high pressure liquid chromatography (HPLC). Although similar to liquid chromatography in theory, efficiency is improved by using a column of tightly packed, small, uniformly sized silica spheres. These spheres ensure a larger surface area for adsorption of the fractions being analyzed. A high pressure pump is required to force the mobile phase through the tightly packed column.

High pressure-gel permeation chromatography (HP-GPC) is a variation of high pressure liquid chromatography. This technique uses the same pumping and detection equipment as HPLC, but uses columns packed with porous styrene gel of known pore sizes, rather than silica gel. This styrene gel does not rely upon adsorption to separate the fractions, but uses the pores in the gel to trap particles passing through the column. Large particles, unable to penetrate the pores, elute from the column first. Smaller particles, which can penetrate further into the gel pores, emerge at progressively later times, based upon their size. This principle of operation gives HPGPC its alternate name, size exclusion chromatography. HPGPC is the only chromatography technique that uses molecular size rather than chemical characteristics to separate a material's fractions.

2.2.2 - HP-GPC Methodology

An HP-GPC system consists of six components:

1. Pump
2. Injector
3. Column
4. Detector
5. Recorder
6. Processing equipment

Figure 2-4 shows a schematic of a typical HP-GPC system, which has the functions described in the paragraphs that follow [7].

The most important function of the pump, or solvent delivery system, is to provide a constant flow of the mobile phase (solvent) through the system under pressure. In order to compare one analysis to another the flow rate and the pressure must be uniform regardless of viscosity differences in the solvent/solution mixture. Changes in flow and/or pressure can produce differences in the extent of penetration of the solution into the gel pore structure.

Injection of the sample can be performed manually or automatically, but must be injected in an accurately measured amount and not disturb the continuous flow of the mobile phase. Completion of the injection usually triggers the detection equipment to begin operation.

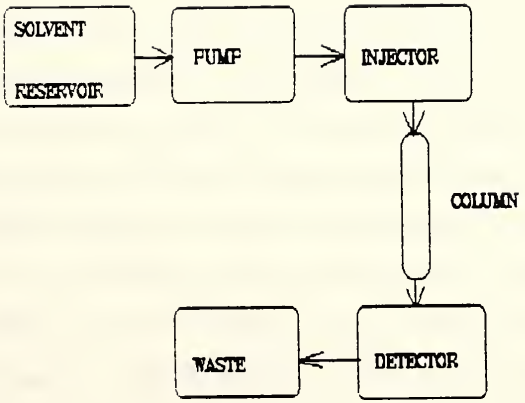

Figure 2-4. Typical HP-GPC System

Following injection, the sample passes into and through the column. HPGPC columns are typically packed with styragel beads of known pore openings of single or multiple sizes. It is important that the mobile phase be compatible with the column packing, as specified by the manufacturer. Columns must provide reproducible information over extended periods of operation, which requires them to be flushed with pure solvent between runs. Column heaters may be used to maintain a constant temperature which will assist solvent flow through the stationary phase.

Detectors can be either refractive index or ultraviolet type. Refractive index detectors are the most widely used detector, and use the principle of light refraction to measure the difference between the refractive index of the mobile phase alone and the refractive index of mobile phase carrying asphalt molecules. The higher the refractive index, the greater the number of asphalt molecules in the mobile phase stream. These detectors are often used in conjunction with an ultraviolet, or UV, detector. UV detectors are set up to measure a specific wavelength or type of material.

Recorders then convert detector signals to a trace on paper, recording the distribution of molecule sizes passing through the detectors. Automatic data processing equipment calculates, records and stores information about the materials characteristics. The recorder and processing

functions can be combined in computer systems that also monitor and control the pump, injector and detectors.

The choices of equipment and operation parameters have major effects on the results, as reported by Glover et al. [8]. The major parameters that can affect results include selection of solvent, columns, and detectors, methods of sample preparation and the chromatogram analysis techniques.

The first set of decisions which affect the results of chromatography involves the choice of mobile phase (solvent) to be used in the system. The two solvents most widely used for chromatography of asphalt are tetrahydrafuran (THF) and toluene. Glover [8] and Jennings [9] reported that THF, being the stronger solvent, permitted samples to elute sooner from the column. The strong polar nature of THF also allows the asphaltene fraction to remain in solution rather than associating with other fractions to form larger agglomerations of molecules. Use of toluene can also cause asphaltene and saturate fractions to be suppressed.

Brule [10] also reported that the association of molecules allowed with the use of THF most closely approximates that association which naturally occurs within asphalt, yet which is within operating parameters of most chromatography equipment. Donaldson et al. [11] reported that THF is the best solvent to use when evaluating properties that depend on asphaltenes, especially those

relating to age hardening.

Sample concentration in the mobile phase also affects the degree of association and the resulting chromatograms [12,13,14]. Although use of a higher than normal concentration can enhance differentiation of the asphalt fractions [8], concentrations must be kept to a level that allows the entire chromatogram to appear on the scale of the recorder. The concentration that works best with a given chromatography system is determined experimentally, and has been reported to be typically 0.5 to 1.0% [15,16].

An additional consideration for the solvent is the time limitation between mixing and injection of the sample. If asphalt remains in a THF solution for more than one hour, the asphalt molecules will continue to break down into smaller molecules which do not represent the natural association found in asphalt [17,13]. According to researchers, this requires that samples be injected less than one hour after preparation.

Column selection and the number of columns used also affects the chromatography results. Column sizes are determined by the pore size, and standard columns are 100, 500, 1000, 10,000, 100,000 and 1,000,000 Angstrom units. Columns are selected to provide a range of pore sizes that will allow a wide range of the asphalt molecules to penetrate into the pore spaces. This will provide different elution times for the molecules and a definable separation of fractions. Asphalt molecules are normally in

the lower range of the column sizes. Although additional columns connected in series provide better fraction resolution, they also increase the time of elution, which must be kept under one hour total from time of sample preparation.

Temperature of the solvent as it passes through the column also affects system performance, and can produce different chromatograms for the same material. Column heaters are recommended to maintain a constant temperature between 25°C to 35°C throughout testing. Care must be taken to ensure that temperatures do not exceed the boiling point of the mobile phase, 66°C for THF [18].

After the solvent and sample elute from the column, the distribution of molecular sizes must be measured. This is accomplished by a refractive index (RI) or ultraviolet (UV) detector. Although other detectors, such as infrared, nuclear magnetic resonance (NMR) and mass spectroscopy, are better suited for detection of the full range of complex hydrocarbon molecules found in asphalt, their expense precludes their use in chromatography research [12].

The refractive index, or differential refractometer as it is also termed, measures the difference between the refractive index of the mobile phase and the refractive index of the stream of asphalt molecules flowing through the detector. The higher the refractive index, the greater the number of asphalt molecules passing the detector. The output plot from the RI detector, then, is a plot of number

of molecules versus time of elution. If an HPGPC system has been calibrated by measuring the elution time of samples of known molecular weight, this plot can be used as a distribution of molecular weights of the asphalt molecules.

Since the RI detector measures the difference between refractive indices, they are insensitive to materials with a refractive index similar to that of the mobile phase. THF has a refractive index of 1.408, while toluene has a refractive index of 1.496. Paraffinic molecules, with a refractive index of 1.500, therefore, are difficult to measure with toluene as the mobile phase. With either solvent, aromatic molecules (RI = 1.650) provide a stronger response than parafinnic molecules [19,20].

Ultraviolet (UV) detectors are not as well suited as RI detectors for detection of asphalt molecules. Work by Jennings [21], in which he simultaneously recorded UV detector responses to asphalt at 220, 254, 340, 410 and 510 nanometer wavelengths, showed that different wavelengths would produce different chromatograms. Jennings also reported that the differences in intensities of the detector's xenon lamp that occur with use also lead to differences in the chromatograms.

Other detectors that have the capability to measure the full range of hydrocarbons in asphalt are infrared, nuclear magnetic resonance (NMR) and mass spectroscopy. These systems are not commonly used in the chromatographic

analysis of asphalt due to their high expense [13].

2.2.3 - Analysis of Chromatograms

The result of chromatographic analysis is a plot of the distribution of molecule sizes, or a count of molecules versus time of elution. A typical chromatogram for asphalt is shown in Figure 2-5. The plot begins with injection of the sample and ends with a characteristic "solvent flush", represented by a negative spike in the curve. The lag between injection and start of the curve represents the time required for the "slug" of sample to reach and elute from the column. It is important that this portion of the plot is flat, to form a stable baseline from which counts are measured [7, 19].

The majority of researchers have divided chromatograms into three equal segments based on the time from start to finish of sample elution [9,22]. These three segments are termed large, medium and small molecular size fractions (LMS, MMS, and SMS, respectively), of an asphalt. The area under the curve within each segment, expressed as a percentage of the total area, is an approximate measure of the amount of asphalt molecules of each fraction eluting from the column. Figure 2-6 shows the division of a typical chromatogram into LMS, MMS and SMS fractions.

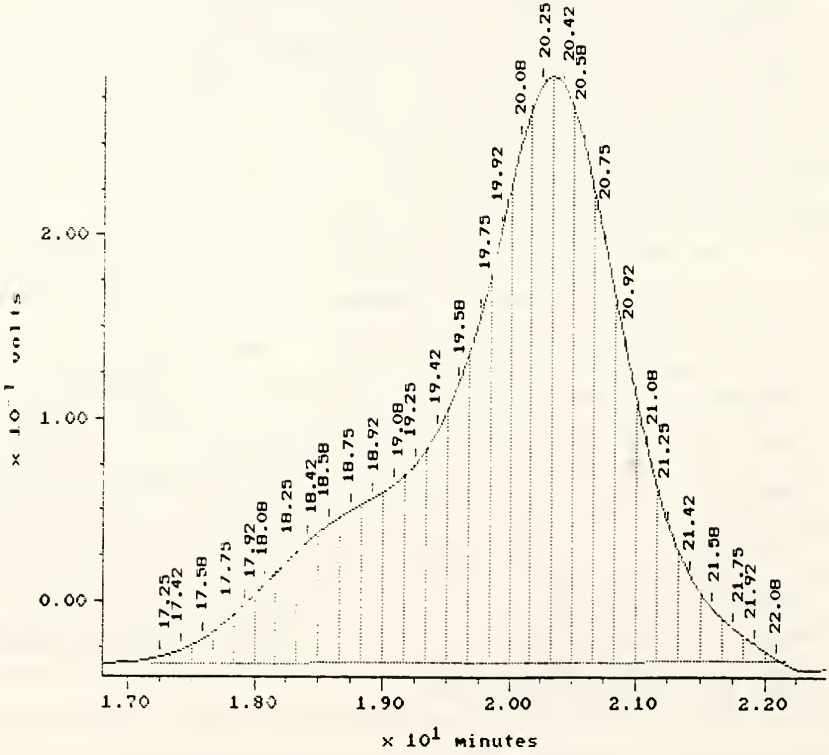

Figure 2-5. Typical Chromatogram of Asphalt

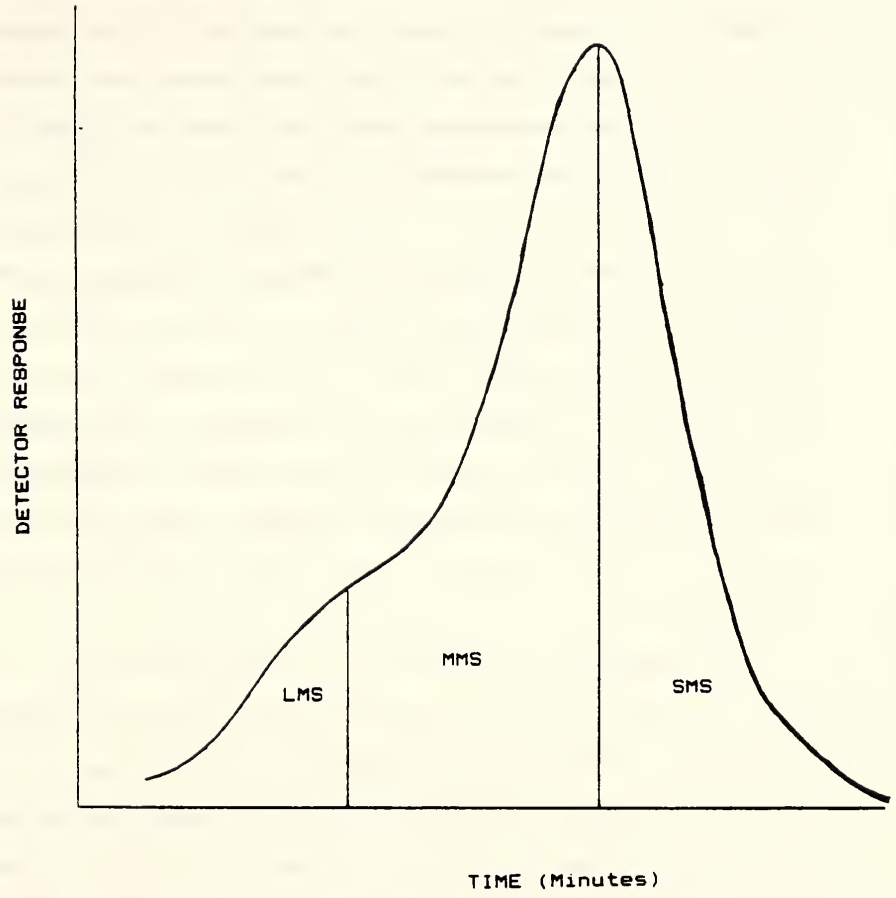

Figure 2-6. Division of Chromatogram into Analysis Segments

Two recent research projects have used divisions other than thirds. Garrick [15] divided chromatograms into eight segments, not based on time divisions, but on the basis of eight equal areas. Price [16,23] used equal time segments, but divided chromatograms into four and ten equal time segments for better resolution of the data. Chollar et al. [24] used sixty slices of equal time for analysis, but divided the total chromatogram into the standard thirds by looking at the appropriate slice out of the sixty total slices for determining the division lines. With the introduction of computer analysis packages, any number of slices can be used for analysis of the chromatograms, depending upon the resolution desired. The greater the number of slices selected, the more accurate the area calculations.

In addition to a molecular size distribution, HPGPC can be used to calculate the molecular weight averages of materials. This requires accurate calibration of the system by passing narrow band molecular weight polystyrene standards through the system. By using a plot of elution time versus molecular weight, regression anlaysis can be used to determine the relationship between elution time and weight.

Molecular weight averages, previously calculated by hand from distribution curves, can be determined by use of specially prepared software programs [7]. These averages, based on a number average or weight average, have been used

in the analysis of polymers [25]. Some general correlations have been developed relating various polymer properties to effects of molecular weight averages [26]. Table 2-2 shows the general correlations that have been developed. Several of the parameters affected by molecular weight averages and distribution have importance in the evaluation of asphalts.

Dougan [27] used weight average molecular size, number average molecular size and a measure of curve spreading, termed polydispersity in his analysis of chromatograms of asphalt age hardening. He determined that these values increase as samples age, and indicated that there could be a strong relationship between these values and asphalt aging.

2.2.4 - HPGPC Research on Asphalts

The HPGPC process was developed in 1963 for analysis of polymers, but was quickly adapted for asphalts. Altgelt [24] was the first to publish research results using this technique on asphalt. This was followed by Richman [28] two years later, and Breen and Stephens [29] in 1969. These studies concentrated on analysis of the components of asphalt, with emphasis on the separation of the asphaltene fraction.

Table 2-2. General Correlations Between Molecular Sizes and Polymer Properties [26]

Property	Increase Molecular Weight	Narrower Distribution
Tensile Strength	+	+
Elongation	+	-
Yield Strength	+	-
Toughness	+	+
Brittleness	+	-
Hardness	+	-
Abrasion Resistance	+	+
Softening Temperature	+	+
Melt Viscosity	+	+
Adhesion	-	-
Chemical Resistance	+	+
Solubility	-	0

Key: + Property increases

\- Property decreases

0 No change

The first chromatography research that attempted to relate chromatograms to asphalt performance was reported by Bynum and Traxler [20] in 1970. They applied gel permeation chromatography to nine asphalt sections evaluated over a three year period from 1963 through 1966. Their research showed that gel permeation chromatography techniques could distinguish differences between asphalts from different crude sources, as well as differences in the same asphalt with aging. The differences in a given asphalt with age were small for asphalts which showed good resistance to age hardening, but pronounced for asphalts showing poor resistance to age hardening. No clear relationship between molecular size and performance was detected, however.

Using the work developed by Bynum and Traxler on gel permeation chromatography, several other researchers continued to refine the procedures. In 1971, Haley [30] studied asphaltenes, and reported that chromatograms suggested that asphaltenes consist of unit sheets linked together, rather than one large aromatic ring, since different sizes of asphaltene molecules were disassociated by different solvents. This conclusion that different solvents produce large variations in apparent molecular size was later verified by Bergmann, Duffy and Stevenson [31].

The most extensive use of high pressure-gel permeation chromatography (HPGPC) for the study of asphalt has been

the work performed by Jennings et al.[9,12,13,17,21,32,33], at the University of Montana. Jennings' studies centered around the characterization of asphalts used in Montana, but have been expanded and applied to asphalts throughout the United States by other researchers. Using the division of the chromatogram into thirds, he defined the three sections of the distribution curve as large molecular size (LMS), medium molecular size (MMS) and small molecular size (SMS).

The LMS fraction, Jennings reported, consists of the asphaltenes and the larger maltene molecules. This may be due partly to the higher molecular weight of the asphaltene molecules, but is largely due to the polarity of the asphaltenes and their tendency to form associated molecular combinations, as reported by Altgelt and Reerink [34,35]. Boduszynski [36] confirmed the hypothesis of this association, reporting that the average molecular weight of the asphaltene fraction is approximately the same as the other generic fractions, but increases only through agglomeration of molecules. Jennings found that the several properties of asphalt, including stiffness, can be related to LMS fraction of the asphalt.

Jennings found from his study that asphalt pavement cracking is related to the relative amount of the LMS fraction [33]. A high amount of LMS fractions was typically found in severely cracked pavements, and a low LMS fraction was desirable for reducing asphalt pavement

cracking. Jennings [21] determined that a finished pavement should have a composition of:

8-10% - LMS

46-48% - MMS

44-46% - SMS

An original asphalt should have a composition of:

6-8% - LMS

44-48% - MMS

46-48% - SMS

This general relationship between chromatograms and cracking was confirmed by Plummer and Zimmerman [37] using pavement samples from Indiana and Michigan, and by Hatlingh [38]. Hatlingh further determined that there is also a minimum amount of the large molecule fraction required to prevent pavement tenderness. Pribanic [39], following up Jennings' study on age hardening [21], did find correlations between chromatograms and temperature susceptibility (PVN) and aging index. Her study did have the advantage of using a more advanced data analysis program than used by the earlier researchers.

Jennings et al. [21] also used HPGPC to evaluate the relationship between molecular fractions and climate or asphalt refining process. They found that there was a correlation between the amount of LMS and climate. Pavements in warmer climates were able to tolerate a larger amount of the LMS fraction than pavements in colder climates. This correlation was verified by Chollar [40],

who performed an expanded statistical analysis of Jennings' data, as well as developing his own original data on the same relationships.

Jennings et al. [21] also found a dependency of molecular size distribution on the asphalt processing. Some of the factors that caused changes in the asphalt chromatograms were the type of refining process, asphalt heating techniques and temperatures, and mixing with aggregate or additives. These factors almost always produced an increase in the amount of large molecules in the asphalt, which ranged from a 20% to 80% increase in large molecular size molecules. From these results, they concluded that the most significant change in an asphalt's chromatogram was caused by processing in the asphalt plant. Recent work by Burr et al. [41] further attributed changes in chromatograms to the fuels used in the processing of the asphalt, especially where diesel fuels were used in drum mix plants. Von Quintas et al. [42] reported a one percent increase in fuel contamination with the use of diesel fuel.

2.3 - Asphalt Plants

2.3.1 - Types of Asphalt Plants

There are predominantly two types of asphalt plants used to produce hot mix asphaltic concrete in Indiana. The older process is the batch plant, which weighs and mixes components in discrete "batches". The second type of plant is the drum mix plant, which continuously proportions the aggregate, heating and drying them in a rotating drum, and

simultaneously mixing them with a controlled amount of asphalt [1]. Introduced in the late 1960's, drum mix plants now account for approximately 95% of new plant sales in the United States [43].

In the batch plant, cold aggregate is fed from the cold bins in the proper proportions set at the cold feed gate. It is carried to the dryer, where it flows toward a burner through an inclined revolving drum equipped with baffles or flights. The flights pick up the aggregate and drop it in veils through the burner flame. The burner heat removes moisture from the aggregate and heats the aggregate to the proper mixing temperature (approximately 300°F).

The hot aggregate, as it leaves the dryer, is transported in the hot elevator to a screening unit. The aggregate is separated into specified sizes by the screens, and is stored in hot bins. Measured amounts of aggregate from the bins are collected in a weigh box, and then dumped into the pug mill where it is mixed with the appropriate amount of hot asphalt cement. Following mixing, the asphalt concrete "batch" is dumped into a truck [44].

The dryer is designed to heat and dry aggregate that has approximately a 5% moisture content. Conditions of lower moisture can yield a higher volume of dried aggregate, while higher moisture will reduce capacity. Both the feed rate and the burner temperature must be adjusted to provide a longer, hotter drying period for wetter aggregates. Most problems in the dryer are a result

of trying to dry wet aggregate or more aggregate than the dryer can handle, which will result in higher moisture contents than desired. A second problem, which is of interest to this study, is caused by incomplete combustion of fuel, adding an oily film to the aggregate and affecting adhesion of the asphalt cement to the aggregate. This problem usually occurs with plants using low grade or recycled fuels. These fuels require adjustments to the velocity of the draft air in order to be properly atomized, and are very susceptible to changes in air and material flow.

The drum mix process was developed to use simplified equipment and procedures to eliminate errors in repeated weighing and batching of materials. The overall flow of materials is approximately the same as in the batch plant, with the exception of the proportioning and the drying/mixing methods. The aggregate is weighed automatically as it is carried on the cold feed conveyor to the drum mixer. This weighing system is interlocked with the asphalt pump, adjusting the blend of materials to changes in the aggregate flow.

The drying/mixing process is what really distinguishes the drum mix plant from the conventional batch plant. This process combines the drying and mixing functions in one piece of equipment. The wet aggregate is fed to the drum-dryer, which can be considered to consist of two zones. In the primary or radiation zone, the aggregate is heated and

dried by the burner flame. In the secondary zone, asphalt is added to the drum and mixed with the heated aggregate. Some continued convection heating takes place in this zone. The two zones are shown in Figure 2-7.

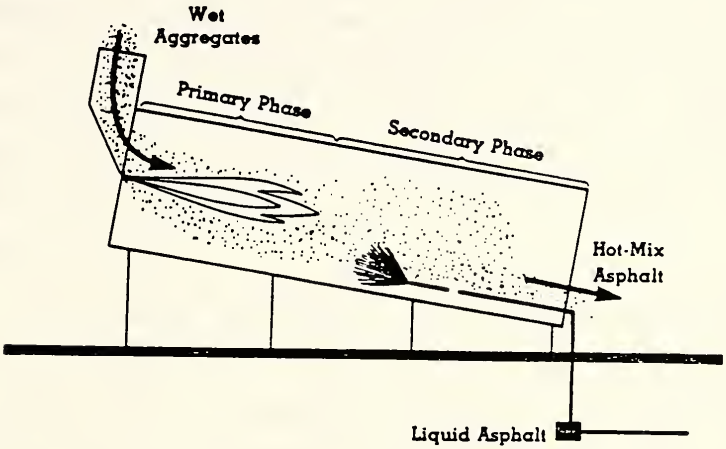

Figure 2-7. Drum Drier Zones

As with conventional dryers, the drum dryer is equipped with flights, which both move the aggregate through the drum and pick it up and drop it in veils through the flame. The burner can be fueled by oil, gas or both, as with conventional batch plant dryers. Since the aggregate passes directly through the flame and there is also a desire to keep the asphalt from being burned, the manufacturers report that the drum dryer can operate at a

lower temperature. Although this can lower fuel costs, it can result in the incomplete combustion of the fuel, and subsequent contamination of the aggregate.

2.3.2 - Differences in Mixes Produced

There are several differences between drum mix and conventional batch plants that can lead to differences in the resulting mix. These have been attributed primarily to the use of the drum mixer to both dry the aggregate and serve as the mixing chamber for the aggregate and asphalt.

The Federal Highway Administration and some state agencies have studied the effects of the drum mix plants on the resulting mix. North Dakota [45] compared laboratory samples with those obtained from drum mix plants, and noted that Marshall mix design parameters were significantly different. Of the mix characteristics that have been reported as being different, two of the most common are asphalt hardening and mix contamination.

When the drum mix process was introduced, there was concern that the proximity of the asphalt to the dryer flame would adversely harden the asphalt. Studies, however, show that the lower mixing temperatures for the drum mix plant actually decreased the hardening rate of the asphalt compared to conventional dryers [46]. Von Quintus and Kennedy [45] showed that hardening in drum mixes was substantially less than would be expected using the Thin Film Oven Test. Studies by Georgia and Maine also support this finding.

A study of two to five year old projects conducted by Terrel and Holen [47] showed that the drum mix process produces less age hardening than conventional plants for several years after placement. The data were normalized as a percent retained penetration because several different asphalts were used on these projects. The study showed that the rate of hardening proceeds at a lower rate for the drum mixes when compared to conventional rates. Studies in Texas, Wyoming and Michigan produced similar results, and lower dryer temperatures were cited as the most logical cause [45,46,47].

Although many studies show that the drum mixers result in less age hardening of the asphalt, studies in California [48] and Oregon [49] indicate that the lower temperatures alone may not be responsible for this result. Their studies and that by Von Quintus and Kennedy [45] indicate that contamination by unburned fuel, especially in the lower grades, may contribute to the softer mix. This softening is more pronounced in drum driers than in conventional driers, and may lead to early rutting. The amount of softening contributed by this contamination versus that contributed by the lower temperature has not been established conclusively by any research performed to this date.

Although the effects of the contamination have not been quantified, many states have specified higher mixing temperatures to ensure that complete combustion is taking

place, or have restricted the type of fuel used in the burner. Oregon, for example, has adopted a requirement that all burner fuels be natural gas, liquified natural gas, fuel oil in grades 1 and 2, butane or propane [46].

In addition to conducting comparisons of mixes produced by both types of plants, the Von Quintus and Kennedy study of 48 projects in seven states [45] compared pavement distress in sections produced by drum mix plants to similar pavement sections produced by batch plants. The study looked at the distress of bleeding and flushing, raveling, rut depth, cracking, roughness and skid resistance. Terrel and Holen's earlier study [47] evaluated five projects for similar distresses.

Although neither study observed any significant difference in rut depth between mixes produced at the two plant types, several agencies have reported early rutting of pavements produced by both plants. This rutting has been speculated as being caused by fuel contamination [45,47] in the driers.

The Von Quintus and Kennedy [45] study also reported more cracking with pavements paved with batch plant produced mixes than with those produced by drum mix plants. When linear cracking was evaluated, a greater amount was observed for batch plant mixes. They attributed this to the difference in asphalt hardening discussed earlier.

Transverse cracking was evaluated in terms of the type of fuel used in the burner. The mixes produced with

"dirtier" fuels exhibited less transverse cracking, possibly due to fuel contamination, or the lower temperature and reduced hardening.

2.4 - Characteristics of Asphalts

Several characteristics of asphalt cements are measured to predict the performance of asphalt mixes. Although not all asphalt characteristics can be correlated to mix performance, among the more commonly used are temperature-susceptibility and resistance to age hardening.

2.4.1 - Temperature Susceptibility

Asphalts are characteristically classified as thermoplastic materials, and thus, their viscosities change with changes in temperature. Asphalts which show large increases in viscosity with temperature decreases have been associated with rutting in warmer climates and thermal cracking in cold climates [50]. In order to limit temperature susceptibility, asphalt specifications set minimum penetration values (25°C) for a given absolute viscosity (60°C) [49]. The higher the penetration for a given viscosity, the lower its temperature susceptibility.

Several other indices are used to measure temperature susceptibility. One of these measures is the penetration viscosity number (PVN), which is an indication of the slope of the viscosity-temperature relationship measured between 25°C (77°F) and 60°C (140°F) [51], using penetration and

viscosity measures, respectively. A low value of PVN indicates a very temperature susceptible asphalt. The equation used to calculate PVN is the following [51]:

$$PVN = \frac{(6.489 - 1.590 \log P - \log V)}{(1.050 - 0.2234 \log P)} * (-1.5)$$

where, P = penetration at 25°C (77°F)
V = viscosity at 60°C (140°F)

PVN can also be calculated using penetration at 25°C (77°F) and viscosity at 135°C (275°F), using the following equation [51]:

$$PVN = \frac{(4.258 - .7967 \log P - \log V)}{(0.7951 - 0.1858 \log P)} * (-1.5)$$

where, P = penetration at 25°C (77°F)
V = viscosity at 135°C (275°F).

Another measure of temperature susceptibility is the viscosity-temperature susceptibility number (VTS), calculated by the following equation [54]:

$$VTS = \frac{\log \log V(T2) - \log \log V(T1)}{\log T1 - \log T2}$$

where, V(T1) = viscosity at 60°C (140°F), in poise
V(T2) = viscosity at 135°C (275°F), in poise
T1 = 333°K (60°C)
T2 = 408°K (135°C)

Large values of VTS indicate greater temperature susceptibility.

A third measure of temperature susceptibility utilizes penetration values measured at two temperatures. Penetration Index (PI) is calculated by the equation [54]:

$$PI = \frac{(20 - 50A)}{1 + 50A}$$

where, $$A = \frac{\log P(T1) - \log P(T2)}{T1 - T2}$$

P(T1) = penetration at 25°C
P(T2) = penetration at 60°C
T1 and T2 = 25°C and 60°C, respectively.

If penetrations are not measured at 60°C, they can be calculated from viscosity values measured at 60°C, using the following equation:

$$P(T2) = \frac{(-5.42 \log (V60/13000)}{8.5 + \log (V60/13000)} - \log 800$$

where, V60 = viscosity at 60°C.

Typical PI values range from +2 to -2. Larger negative values indicate greater temperature susceptibility. Puzinauskas [54] has indicated that VTS and PVN have more repeatable values and have wider acceptance than does the use of PI.

Anderson and Dukatz [22] and Button et al. [55] studied the relationship of penetration index, viscosity temperature susceptibility and penetration viscosity number

with chemical composition. Although neither investigator could establish a relationship, Thenoux et al. [56] indicated that the earlier studies treated original and field samples together, while his analysis indicated that these asphalts should be treated separately. Although Goodrich and Dimpfl [50] found that a relationship between temperature susceptibility and an asphalt's chromatogram was weak, Garrick [15,57], in comparing temperature susceptibility and chromatograms, found that distinct relationships did exist between the asphalt and its temperature susceptibility measure. Price [16] also reported a strong correlation between chromatograms and penetration viscosity number and viscosity-temperature susceptibility values.

2.4.2 - Age Hardening

Asphalts age harden through time with exposure to oxygen and heat. The amount that an asphalt hardens can affect the mix behavior during lay down and compaction and pavement durability. Age hardening occurs in two distinct stages. The first stage of age hardening occurs during the asphalt mix production process. The normal method of measuring this age hardening is through comparison of the viscosity of the original asphalt at 60°C (140°F) to that of the asphalt after laboratory aging in a thin film oven [58]. The amount of age hardening is limited in specifications by setting a limit on the Viscosity Ratio, the ratio of asphalt viscosity at 60°C (140°F) after thin

film oven testing divided by its original viscosity at 60°C. Values of Viscosity Ratio normally range from 2 to 6 [50,58].

Other measures of age hardening during the mix production process include measuring the ratio of viscosity at 135°C (275°F) before and after thin film oven exposure, and measuring penetrations before and after exposure. Measurements of penetration are characterized as penetration retained at 77°F or 39.2°F.

The second stage of age hardening occurs during pavement life through exposure to the environment. This age hardening is not controlled by specifications, but is taken into account in normal design procedures.

Studies of the age hardening of asphalts have indicated that the age hardening of asphalt in the laboratory is closely correlated to the aging of asphalt taken from cores [50,58]. Garrick [15] found that there is a correlation between chromatograms and asphalts aged at higher temperatures, as did Stock [59] and Dougam [27]. In an extension of prior work, Garrick and Biskur [60] discovered that the best correlation between GPC parameters and age hardening is between viscosity ratio and the smallest tenth fraction of molecular size. They felt that this supported the hypothesis that asphalts with more volatiles, which would correspond to the smaller molecular sizes, are more likely to show significant age hardening.

CHAPTER 3

EQUIPMENT AND MATERIALS

The principal equipment used in this project consisted of a high pressure-gel permeation chromatography (HPGPC) system for the analysis of the asphalts and burner fuels. Additionally, equipment for testing the physical parameters of asphalt cements, and extraction and recovery of asphalt from compacted mixes and cores were utilized. This equipment and the test procedures are described in the first part of this chapter. The remainder of the chapter describes the materials that were evaluated in this study.

3.1 - High Pressure Gel Permeation Chromatography

3.1.1 - Equipment

The system used for high pressure gel permeation chromatography (HPGPC) was manufactured by Waters Chromatography Division of Millipore Corporation. It consisted of a model 590 solvent delivery system, a U6K injector, and both a model 410 refractive index (RI) detector and a model 440 ultraviolet (UV) detector. Only data from the RI detector was used for analysis, due to the fact that the concentration of sample required to obtain acceptable response from the UV detector was below the

level recommended by other researchers [31,32,61]. Garrick [15] also indicated that the sensitivity of the UV detector was higher than that of the RI detector, requiring careful measurements of concentration, and fluctuations in detector response. Use of only one detector also increased the data storage capacity of the computer.

Instead of a bank of columns connected in series as used by Jennings and other researchers, and discussed in Chapter 2, one linear ultrastyragel column was used. The linear column was packed with ultrastyragel beads with a molecular weight measurement ranging from 2000 to over 4m molecular weight. This corresponds to a bank of 100 Angstrom through 10^5 Angstrom unit columns connected in series. The advantage of this singular column over the previously used series of columns is that it is easier to replace and allows faster elution times. The column was maintained at a constant temperature of 30°C, as recommended by the manufacturer, by use of a column heater controlled by the RI detector.

The system was connected to an IBM AT computer loaded with the Dynamics Solution Maxima 820 software package by means of a system interface module (SIM). This software package controlled all components of the HPGPC system, as well as collection and analysis of data. A schematic of the HPGPC system is shown in Figure 3-1, and a photograph of the system is shown in Figure 3-2.

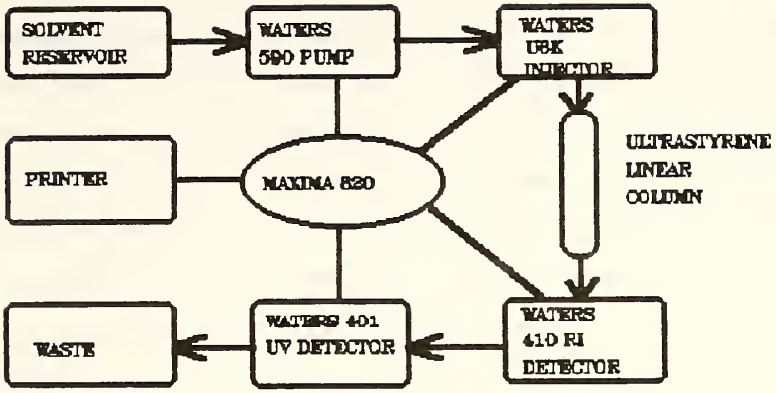

Figure 3-1. Schematic of HPGPC System

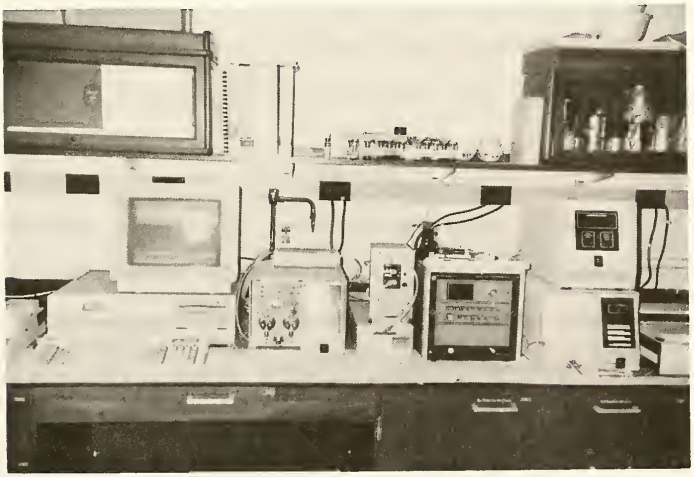

Figure 3-2. HPGPC System Used in Study

3.1.2 - Calibration

The efficiency of the column and the sensitivity of the RI detector were monitored through calibration of the system at the beginning, during testing and at the end of the data collection period. Calibration was performed by injecting eight commercially prepared narrow weight band polystyrene standards that spanned the predicted weights of asphalt and measuring the elution time for each of the standards. In accordance with the manufacturer's recommendations, no more than three standards were injected at one time. Standards in any one injection differed in molecular weight by an order of magnitude for responses to be readily visible. Total concentration of the samples was not more than 1.0% (wt./vol.). Consistency of elution time readings over the course of the testing period is shown in Table 3-1. Full calibration results, including regression equations and curves, are presented in Chapter 4.

3.1.3 - Procedures

Chromatography was performed following procedures developed by Jennings [61], Garrick [15] and Price [16], with modifications based on the performance characteristics of the specific equipment used in this study. Samples were prepared immediately prior to the time of injection in order to ensure that excessive disassociation of molecules would not affect the chromatograms [62]. A time limit of one hour from sample preparation was initially used in this study in order to minimize the adverse disassociation

Table 3-1. Peak Elution Times for Standards

	Date of Calibration			
Standard (Mol. Wt)	2/6	2/13	2/23	3/1
2,700,000	13.08	13.08	13.13	13.11
470,000	14.86	14.92	15.11	15.13
200,000	15.27	15.28	13.35	15.37
110,000	16.42	16.31	16.57	16.51
35,000	16.95	16.96	17.03	17.21
15,000	19.09	19.07	19.10	19.15
3,600	19.21	19.21	19.47	19.51
2,350	19.86	19.67	20.01	19.93

reported by other researchers.

Samples were prepared by dissolving between 0.02 and 0.04 grams of asphalt in a sufficient volume of HPLC grade tetrahydrofuran (THF) taken from the draw-off valve of the system pump to provide a 1.0% (w/v) solution. The sample was agitated to ensure that the asphalt was completely dissolved in the THF. This sample was then filtered through a 0.5 micron pre-injection filter to remove any particles that could contaminate or clog the pore spaces in the column. After filtering, a 100 microliter sample was injected into the injection port of the U6K injector.

Flow through the HPGPC system was maintained at 1.050 ml/min at a temperature of 30°C. The flow rate was accelerated slightly from the recommended rate of 1.00 due to a vibration in the pump that developed at 1.00 ml/min. Each sample run required 25 minutes from the time of injection to completion of data acquisition. This time period ensured that the sample would completely elute from the column and the signal would return to baseline for approximately 5 minutes prior to making a subsequent injection. This return to baseline was essential to ensure accurate measurement of the early eluting molecules.

Data were collected and stored by the Maxima 820 system for further analysis.

3.1.4 - Chromatogram Analysis

As the sample elutes from the column, the detectors measure the amount of sample passing the detector source. This provides a profile of the molecular size distribution for the material injected into the system. This profile was stored by the Maxima 820 software package for analysis and printout. A sample chromatogram printout is shown in Figure 3-3.

The molecular size distribution curve was first evaluated visually for curve shape and peak elution time. The chromatogram was then sliced into five second intervals for area calculations, and slices were grouped so that the chromatogram was divided into thirds, according to the practice recommended by Jennings [12,61]. Additionally, the chromatogram was analyzed to determine molecular weight averages and polydispersity, as will be discussed in more detail in Chapter 4. A sample chromatogram, divided into partitions is shown in Figure 3-4.

3.2 - Asphalt Cement Tests

The first test performed on the original asphalt was measurement of specific gravity, performed in accordance with procedures of ASTM D-70. Absolute and kinematic viscosity tests were then performed at 60°C (140°F) and 135°C (275°F), respectively. The equipment used to perform viscosity tests is shown in Figure 3-5. Penetration tests were also performed on the original asphalt, using a 100g. weight for five seconds, at 25°C (77°F) (Figure 3-6). The

MAXIMA (c) 1987 Dynamic Solutions Division of Millipore

MAXIMA 820 GPC ANALYSIS REPORT

Printed: 16-JUL-1990 9:37:50

SAMPLE: af2orig
Type : UNKN
#1 in Method : ASPHALT HP-GPC
Instrument : Instrument 1
Acquired : 8-MAY-1990 14:24
Filename : af2orig
Rate : 2.000 points/sec
Index : Disk
Duration : 15.000 minutes
Injection Volume : 100.000
Operator : tbn

ANALYSIS PARAMETERS:
Processing Start : 8.25 minutes
Baseline Start : 5.00 minutes
Processing End : 11.00 minutes
Baseline End : 14.00 minutes
Number of Slices : 33
Slice Width : 5.00 seconds

DETECTOR: waters 410 RI

Molecular Weight Distribution Averages:
Number Average : 436
Polydispersity : 9.026230
Weight Average : 3939
Z avg / Wt avg : 4.054788
Z Average : 15974
Z+1 avg / Wt avg : 7.824952
Z+1 Average : 30826

Peak Maximum:
Slice # : 17
Molecular Wt : 2035

Slice Detail:

Slice #	Ret Time (minutes)	Molecular Wt	Slice Height (microvolts)	Slice Area (microvolt-sec)	Cumulative Area Pcnt
1	8.29	72279	4552	23846	0.05
2	8.37	59261	15735	80376	0.20
3	8.46	48456	33394	168039	0.52
4	8.54	39509	56261	281814	1.05
5	8.62	32119	82227	411496	1.83
6	8.71	26032	110114	550568	2.87
7	8.79	21031	138572	693120	4.18
8	8.87	16934	167802	839896	5.77
9	8.96	13589	199866	1000908	7.67
10	9.04	10866	238025	1192423	9.92
11	9.12	8656	287063	1438706	12.65
12	9.21	6870	353068	1769474	15.99
13	9.29	5431	441919	2214202	20.19
14	9.38	4276	554533	2775757	25.44
15	9.46	3353	680463	3400125	31.87
16	9.54	2618	793444	3957192	39.36
17	9.63	2035	858286	4277129	47.46
18	9.71	1575	855930	4267010	55.53

Figure 3-3. Sample HPGPC Printout

19	9.79	1213	796190	3971696	63.05
20	9.88	930	700945	3502593	69.68
21	9.96	709	598186	2992063	75.34
22	10.04	538	501230	2510083	80.09
23	10.13	406	419496	2101533	84.07
24	10.21	305	352472	1764947	87.41
25	10.29	228	294744	1474895	90.20
26	10.38	170	242073	1211129	92.50
27	10.46	125	196171	983372	94.36
28	10.54	92	163984	821588	95.91
29	10.63	67	141191	706299	97.25
30	10.71	49	119019	592972	98.37
31	10.79	35	86567	432001	99.19
32	10.88	25	49890	254662	99.67
33	10.96	18	33619	173513	100.00
TOTAL				52835428	

Figure 3-3. Continued

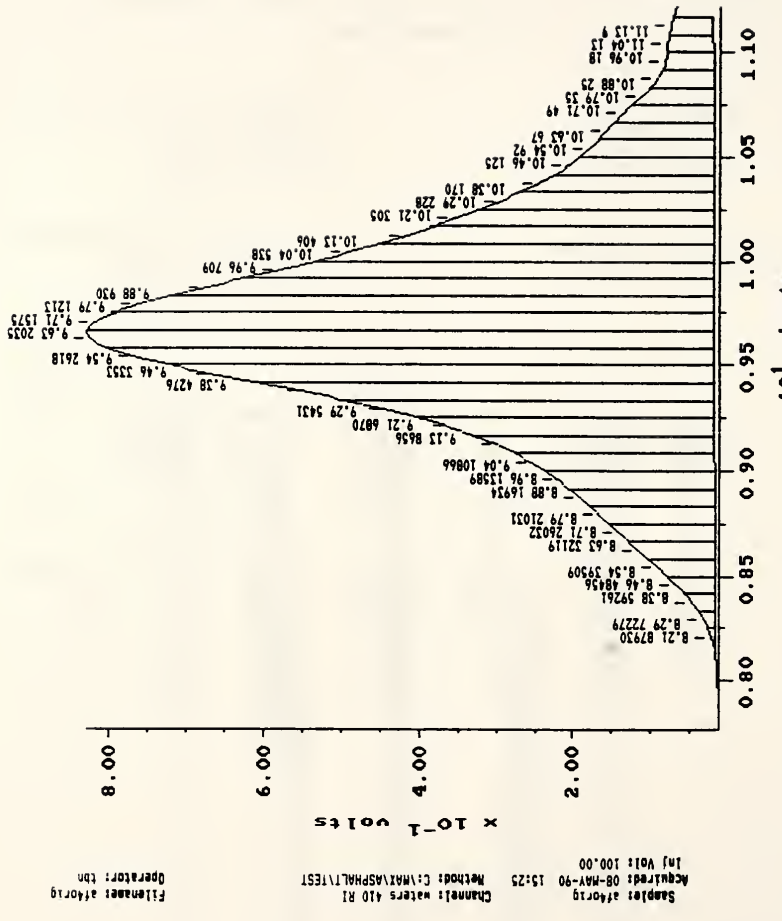

Figure 3-4. Sample Chromatogram

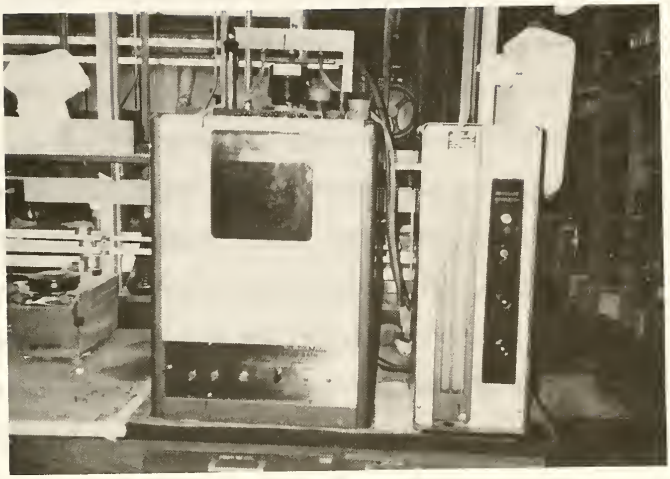

Figure 3-5. Viscosity Testing Equipment

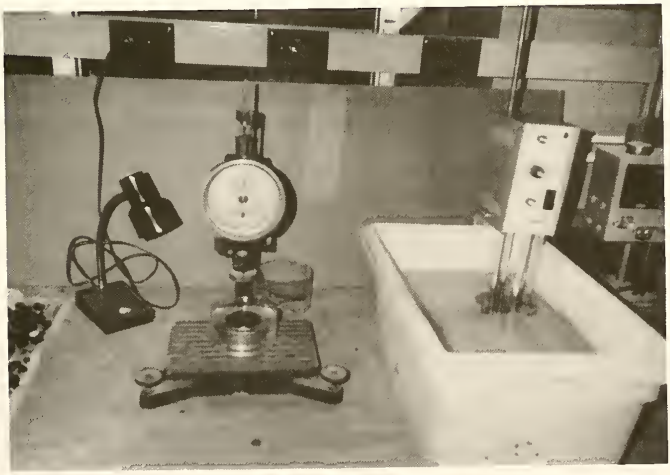

Figure 3-6. Penetration Equipment

results of these tests were used to determine the values of temperature-susceptibility:penetration-viscosity number (PVN) and viscosity-temperature susceptibility (VTS).

After completion of the physical tests on the original asphalt, samples were subjected to the thin film oven test. Asphalt samples were exposed to a temperature of 325°F (163°C) for 5 hours, in accordance with ASTM Specification D-1754. Samples were weighed before and after exposure, to determine loss after heating. Penetration and viscosity values were obtained on the exposed asphalts, as described in the preceding paragraph. Results of the penetration and viscosity tests following thin film oven exposure were compared to the values obtained on the original asphalts in order to derive the index values for age hardening: Viscosity Ratio and Retained Penetration.

A summary of the asphalt parameter tests and the equations used to determine index values of temperature susceptibility and age hardening are shown in Tables 3-2, 3-3 and 3-4, respectively.

Table 3-2. Tests Performed on Asphalt Cements

Test	ASTM Number
Specific Gravity, 25°C (77°F)	D70
Penetration, 25°C (77°F), 100g, 5 sec	D5
Absolute Viscosity, 60°C (140°F)	D2171
Kinematic Viscosity, 135°C (275°F)	D2170
Thin Film Oven Test (TFOT)	D1754
Penetration after TFOT	D5
Absolute Viscosity after TFOT, (140°F)	D2171
Kinematic Viscosity after TFOT, (275°F)	D2070

Table 3-3. Equations for Temperature Susceptibility

1) $$PVN = \frac{(6.489-1.590 \log P - \log V(T1))}{(1.050-0.2234 \log P)} \quad *(-1.5)$$

where, P = penetration at 25°C (77°F)
V(T1) = viscosity at 60°C (140°F)

or

2) $$PVN = \frac{(4.258-0.7967 \log P - \log V(T2))}{(0.7951-0.1858 \log P)} \quad *(-1.5)$$

where, P = penetration at 25°C (77°F)
V(T2) = viscosity at 135°C (275°F)

3) $$VTS = \frac{\log \log V(T2) - \log \log V(T1)}{\log T1 - \log T2}$$

where, V(T1) = viscosity at 60°C (140°F), in poise
V(T2) = viscosity at 135°C (275°F), in poise
T1 = 333°K (60°C)
T2 = 408°K (135°C)

(1 Cst * .95 = 1 poise)

Table 3-4. Equations for Age Hardening

1) $$\text{Viscosity Ratio at 140°F} = \frac{\text{Vis(140) of TFOT Residue}}{\text{Vis(140) of original asphalt}}$$

2) $$\text{Viscosity Ratio at 275°F} = \frac{\text{Vis(275) of TFOT Residue}}{\text{Vis(275) of original asphalt}}$$

3) $$\text{Pen retained at 77°F} = \frac{\text{Pen(77) of TFOT Residue}}{\text{Pen(77) of original asphalt}}$$

3.3 - Asphalt Mix Tests

The INDOT asphalt mixes from the 1985 paving season had been stored in sealed containers in the laboratory. Stored samples were compacted using a mechanical drop hammer weighing 10 pounds. 75 blows were applied to each side of the specimen to produce a 4 inch diameter briquette with a height of approximately 2-1/2 inches. The mechanical compactor, shown in Figure 3-7, was used to compact the mixes.

Specimens were then characterized using Marshall test equipment and indirect tension testing equipment. The Marshall testing equipment is shown in Figure 3-8. This apparatus applies a load at the rate of 2.0 inches per minute to the specimen, which has been conditioned at 140°F for 30 to 40 minutes. The applied load and the vertical deformation of the specimen are recorded on a chart recorder. The maximum load applied to a sample brought to failure is termed Marshall stability. This value was corrected for briquette thicknesses that were not exactly 2.5 inches. The briquette's deformation or the shortening of the vertical diameter from the beginning of load application until failure (load drops off) is recorded as Marshall flow. A sample graph depicting these measurements is shown in Figure 3-9.

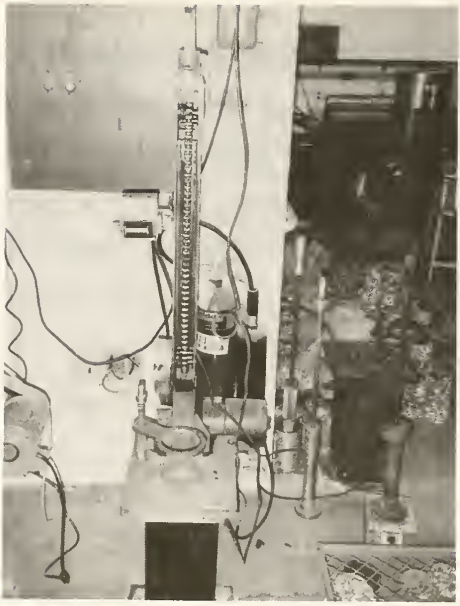

Figure 3-7. Mechanical Compactor

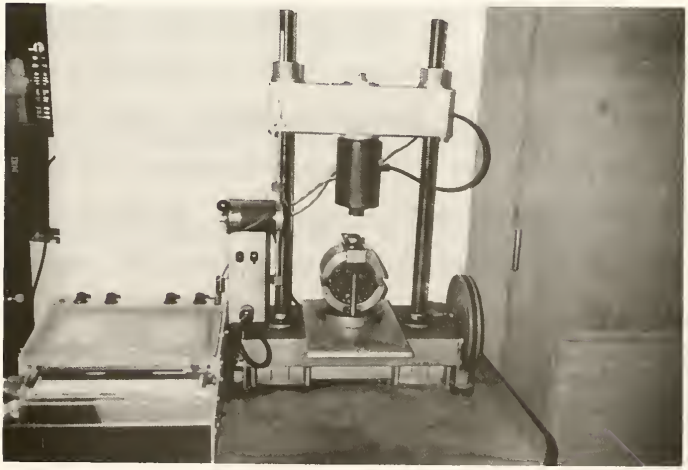

Figure 3-8. Marshall Testing Equipment

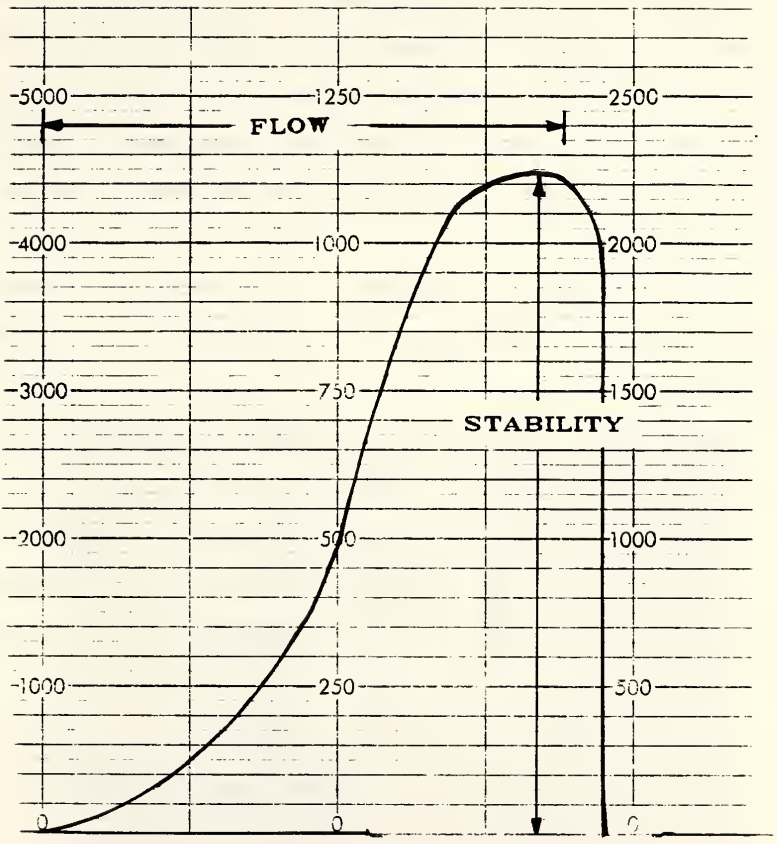

Figure 3-9. Sample Marshall Data

Indirect tension testing was performed using the Marshall testing apparatus, but with an indirect tension head replacing the Marshall head. The indirect tension head was fitted with 0.5 inch wide loading strips at the top and bottom. The loading strips had concave surfaces to conform to the shape of the test specimen. Marshall apparatus fitted with the indirect tension head is shown in Figure 3-10.

Standard Marshall specimens are used for indirect tension testing. Testing was conducted at an ambient temperature of approximately 74°F. Loading was applied at a rate of 2 inches per minute. A chart recorder was used to provide a record of load versus vertical deformation of the specimen. The maximum load at failure, as determined from the chart recorder, was used to calculate the tensile strength of the material. The following equation was used [63]:

$$\text{Tensile strength (psi)} = \frac{(0.156\ P)}{t}$$

where, P = total load at failure (pounds)
t = height of specimen (inches)

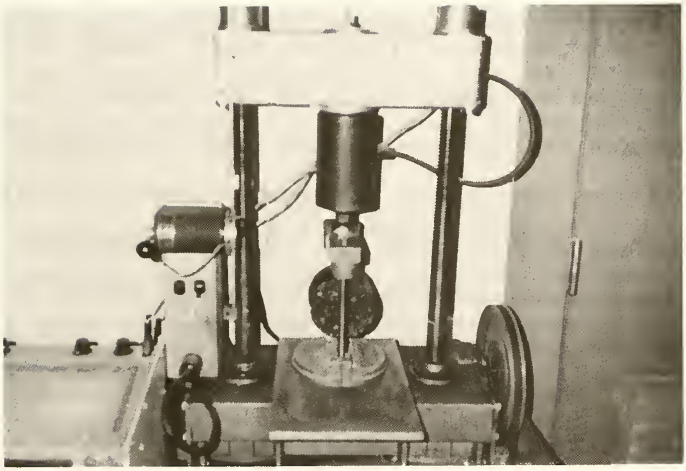

Figure 3-10. Indirect Tensile Test Equipment

3.4 - Materials

3.4.1 - Asphalt Cements

Asphalt cements included in this study were all AC-20 grade asphalt cements collected during the 1985 paving season. This is the grade most commonly used by the Indiana Department of Transportation during that paving season. Sixteen samples were tested and represent the largest suppliers of asphalt to Indiana in the 1985 paving season, and represent Indiana, Illinois, Ohio and Kentucky suppliers.

Changes in asphalt cements caused by processing methods, were evaluated from an equal number of samples from both batch plants and drum mix plants. A second consideration was the type of fuel used to heat and dry the aggregate for both types of plants. The combination of plant type and fuel used are major determinants of the drying temperature and combustion (exhaust draft) settings. These parameters can contribute to fuel contamination caused by incomplete combustion of the fuel and age hardening of the asphalt, as discussed in Chapter 2. Both of these are factors which were to be evaluated in this study. A sample identification system was developed for this study. The samples are designated first by the letter that corresponds to the fuel type used in the dryer: "G" for natural gas, "R" for reclaimed oil, "T" for number 2 grade burner fuel, and "F" for number 4 grade burner fuel. The numbers 1 through 4 designate the number of the sample

within each fuel type. Table 3-5 shows the breakdown of samples by asphalt plant type and fuel type.

All samples were collected prior to mixing at the asphalt plant supplying material to the individual paving projects, and were sealed in metal quart containers. These samples were delivered to Purdue University immediately after collection, where they were stored at an ambient temperature of approximately 72°-74°F until tested. Prior work by Price [16] and Thenoux [56] indicates that such storage of samples has little effect on the chromatograms produced from the asphalt. The asphalt cements used in the project, and their suppliers are listed in Table 3-6.

The physical properties of the asphalt cements, as described in Section 3.2, are given in Table 3-7.

3.4.2 - Asphalt Mixes

Asphalt concrete mixes, as with the asphalt cements, were collected during the 1985 paving season and stored at Purdue University in sealed containers until tested. Each asphalt concrete mix corresponds to the sixteen asphalt cement samples, representing the mix prepared with that asphalt cement at the particular asphalt plant. The samples selected represent mixes produced by both the batch plant and the drum mix process.

Table 3-5. Plant and Fuel Type for Samples

	Fuel Used in Drier			
	Gas	#2 Burner Fuel	#4 Burner Fuel	Reclaimed Oil
Batch Plant	G1,G2	T1,T3	F1,F3	R1,R4
Drum Mix Plant	G3,G4	T2,T4	F2,F4	R2,R3

Table 3-6. Asphalt Cements and Suppliers

Sample Number	Grade	Supplier	State Code
G1	AC-20	Marathon	7155
G2	AC-20	Ashland	7104
G3	AC-20	Koch Asphalt, North Bend	7142
G4	AC-20	Koch Asphalt, Chicago	7143
R1	AC-20	Marathon	7155
R2	AC-20	Texaco	7118
R3	AC-20	Texaco	7118
R4	AC-20	Marathon	7155
T1	AC-20	Asphalt Materials	7105
T2	AC-20	Chevron	7107
T3	AC-20	AMOCO, Whiting	7101
T4	AC-20	Chevron	7107
F1	AC-20	Koch, Chicago	7146
F2	AC-20	Asphalt Materials	7105
F3	AC-20	Koch Asphalt, North Bend	7142
F4	AC-20	Asphalt Materials	7105

Table 3-7. Physical Parameters of Asphalt Cements

Sample	Specific Gravity	Penetration	Visc. (140°F)	Visc. (275°F)
G1	1.0275	67	2395.7	418.2
G2	1.0255	68	2554.9	328.1
G3	1.0258	57	2273.6	374.9
G4	1.0264	78	2070.1	384.2
R1	1.0258	75	2417.9	415.1
R2	1.0398	58	2206.4	374.9
R3	1.0253	71	2993.6	407.1
R4	1.0247	74	2170.1	426.5
T1	1.0222	54	2377.5	361.3
T2	1.0264	72	2199.8	405.8
T3	1.0237	50	2428.8	404.1
T4	1.0234	64	3050.6	408.5
F1	1.0332	63	3511.6	305.9
F2	1.0143	56	3079.7	363.6
F3	1.0262	64	2348.3	386.9
F4	1.0369	52	2791.4	311.9

Type of mix was a second determinant in the study. Samples were selected to represent the same material (asphalt grade and aggregate gradation) as much as was feasible. Due to the limited number of samples collected during the 1985 paving season, different aggregate gradations and mix type (pavement layer) had to be selected in order to provide enough samples representing each type of asphalt plant and burner fuel. The mixes used and the type of plant producing these mixes are given in Table 3-8. Asphalt was extracted from the mix using trichloroethylene (TCE) in a Rotorex extractor (ASTM D-2172) and recovered by the Abson method (ASTM D-1856). Physical properties of the extracted asphalt cement are given in Table 3-9.

3.4.3 - Burner Fuels

Study samples were selected to represent mixes produced by asphalt plants using the four most commonly used burner fuels: natural gas, number 2 burner fuel, number 4 burner fuel and reclaimed oil. Four samples were selected for each type of burner fuel. A sample of the burner fuel used in the asphalt plant that produced the asphalt mix was collected at the asphalt plant at the time of mix production, and stored in sealed containers for chromatograph analysis. No natural gas samples were collected, since there are no procedures available to test and compare natural gas samples using chromatography.

Table 3-8. Asphalt Plant Types and Mixes

Sample	Type Plant	Type Mix
G1	Batch	#11 Surface
G2	Batch	#11 Surface
G3	Drum	#11 Surface
G4	Drum	#8 Binder
R1	Batch	#5 Base
R2	Drum	#9 Binder
R3	Drum	#5 Base
R4	Batch	#9 Binder
T1	Batch	#9 Surface
T2	Drum	#8 Binder
T3	Batch	#9 Surface
T4	Drum	#8 Binder
F1	Batch	#11 Surface
F2	Drum	#9 Surface
F3	Batch	#9 Surface
F4	Drum	#11 Binder

Table 3-9. Parameters of Asphalt Extracted from Mixes

Sample	Penetration	Visc.(140°F)	Visc.(275°F)
G1	56	5129.5	523.8
G2	71	6084.2	667.6
G3	37	7507.4	634.3
G4	62	4999.0	665.2
R1	54	7875.0	850.2
R2	34	5870.7	521.9
R3	42	10857.8	801.6
R4	42	9790.4	804.3
T1	48	4358.6	520.5
T2	60	8189.3	597.7
T3	34	10496.1	633.4
T4	43	10846.0	752.4
F1	54	4728.2	428.6
F2	60	6179.1	469.4
F3	49	10797.3	1088.0
F4	41	6665.3	574.9

3.4.4 - Cores

Cores from the in-service pavement produced by each mix in this study were collected in 1990 from each of the projects. All project locations were evaluated prior to core site identification to ensure that all pavements were comparable. The PAVER system of evaluation was used to conduct the evaluations [64]. All locations received Pavement Condition Index (PCI) values of greater than 70. The scores for each of the pavement sections are provided in Table 3-10. Photographs of a typical section are provided in Figure 3-11.

Four cores were taken from each project location; two at the edge of the pavement and two between the wheel paths. These coring locations were selected to avoid contamination of the asphalt by fuel spillage by vehicles. To further minimize this possibility, the top 1/4 inch of the core was removed and discarded prior to extracting the asphalt. Although removal of the top 1/4 inch helped minimize contamination, it also removed the asphalt which experiences the most severe in-service aging. Asphalt extracted from the cores for testing of aging were not, therefore, indicative of the maximum in-service aging in the asphalt layer. Locations of the projects are shown in Figure 3-12. Asphalt cement was extracted from the cores using the Rotorex extractor (ASTM D-2172) and recovered by the Abson method (ASTM D-1856). Physical parameters of the recovered asphalt are shown in Table 3-11.

Table 3-10. PCI Ratings of Core Sections

Sample	Location	PCI
G1	SR 250 Jackson City	74
G2	SR 111 New Boston	85
G3	Madison State Hospital	78
G4	SR 37 Monroe County	75
R1	SR 9 Bartholomew County	79
R2	SR 56 Pike/Dubois County	87
R3	SR 241 Knox County	76
R4	SR 60 Washington County	76
T1	SR 25 Tippecanoe County	78
T2	SR 3 Rushville	77
T3	SR 43 West Lafayette	80
T4	SR 350 Ripley County	74
F1	I-74 Fountain County	75
F2	SR 234 Fountain County	71
F3	SR 48 Dearborn County	78
F4	US 41 Parke County	86

Figure 3-11. Typical Pavement Section Sampled

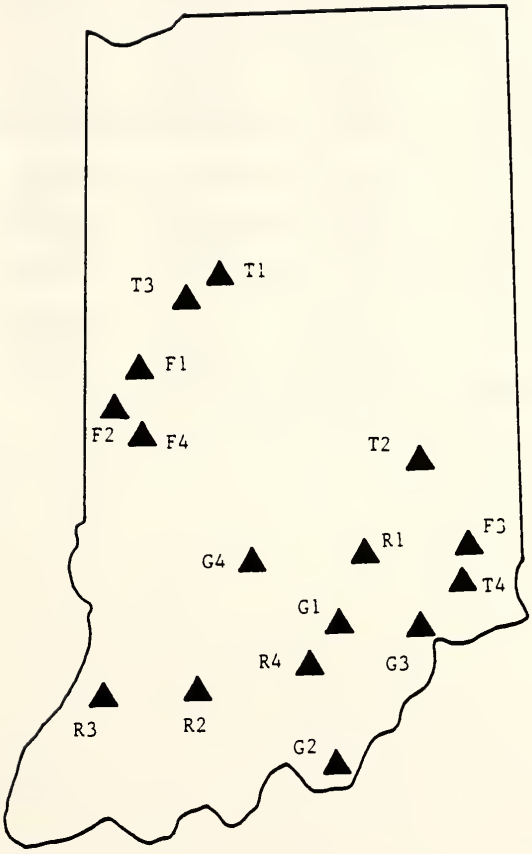

Figure 3-12. Locations of Projects Sampled

Table 3-11. Physical Parameters of Asphalt Extracted from Cores

Sample	Pen	KVis	AVis	PVN	VTS
G1	13	1587.1	12704	-0.41	1.26
G2	9	2345.2	21907	-0.29	1.28
G3	15	1598.5	13673	-0.28	1.29
G4	15	1240.3	18979	-0.57	1.63
R1	11	1512.8	14222	-0.60	1.35
R2	18	2043.6	11129	-0.62	1.48
R3	12	1935.3	22135	-0.26	1.41
R4	12	1453.9	16960	-0.57	1.47
T1	23	899.4	14017	-0.58	1.71
T2	24	816.9	11123	-0.66	1.66
T3	16	1195.4	15149	-0.56	1.54
T4	21	868.2	11597	-0.70	1.63
F1	25	775.8	9781	-0.69	1.63
F2	17	894.9	14120	-0.84	1.71
F3	12	1552.8	17778	-0.50	1.45
F4	26	871.5	12153	-0.51	1.66

CHAPTER 4

OUTLINE OF EXPERIMENT

This chapter consists of two sections. The first section presents a description of the procedures used to test and analyze the samples and the resulting data. The second section discusses the experimental design and analysis of data.

4.1 Test and Analysis Procedures

The organization of the study is shown in Figure 4-1. Original asphalt samples were tested for penetration, viscosity (140°F and 275°F), and specific gravity. Samples were also subjected to the thin film oven test (TFOT). These TFOT samples were subsequently evaluated for loss on heating, penetration and viscosity. Both original and TFOT samples were analyzed using HPGPC procedures.

Samples of the stored mix were divided. The asphalt from one portion was extracted and recovered by the Abson method. This recovered asphalt was tested for penetration and viscosity, and then analyzed by HPGPC methods. The second portion of each mix, approximately 2500 grams, was set aside for fuel contamination testing. A sample of the extracted asphalt was reserved for contamination testing.

Testing of the original samples was completed by

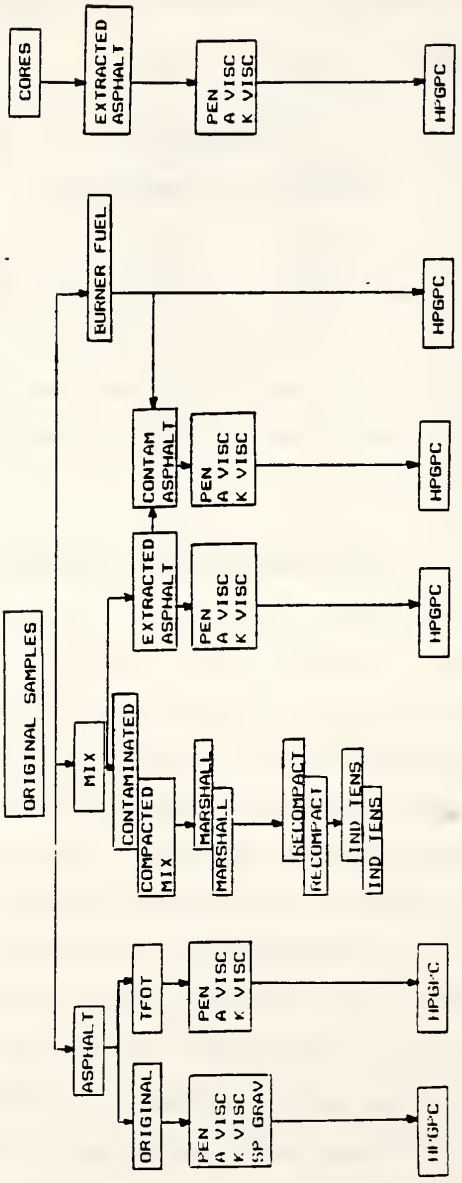

Figure 4-1. Organization of Experiment

extracting and recovering the asphalt from the cores. This recovered asphalt was characterized for penetration and viscosity. These asphalts were then analyzed by HPGPC.

Contamination testing was conducted in three steps. The first step was HPGPC analysis of the burner fuels used to produce the mixes. These burner fuels were then added to the asphalt extracted from the mixes.

A fuel contamination level of 1% was selected based on plant efficiencies reported by Astec Industries [65]. Asphalt plants must operate at a fuel wastage rate of less than 5% to keep emissions within environmental limits. A plant producing 300 tons per hour at 6% asphalt content would use 4235 gallons of asphalt per hour. Using an average fuel consumption rate of two gallons per ton and 5% inefficiency, 30 gallons of fuel would go into the mix each hour. This would represent less than 1% fuel contamination.

The second step consisted of testing this contaminated asphalt for physical properties of penetration and viscosity and HPGPC characteristics. The last step consisted of compacting Marshall briquettes of uncontaminated and contaminated mix. Mixes were contaminated with the same burner fuels and level of contamination as with the asphalt cements. The compacted briquettes were tested for Marshall stability and flow, remolded, and tested for indirect tensile strength. Remolding was required due to the small quantity of mix collected in 1985.

The measured physical properties were used to characterize age hardening and temperature-susceptibility. These measures included penetration viscosity number (PVN) and viscosity temperature susceptibility (VTS), retained viscosity and retained penetration.

Two activities were accomplished prior to the chromatographic analysis of the samples. The first was an evaluation of the repeatability of the process. The second was the development of a calibration curve and regression equation for the equipment and settings used for sample analysis. Repeatability was evaluated by testing and comparing four samples of asphalt from one asphalt source taken at one week intervals for four weeks. These samples were collected during May and June, 1989 from a project on Interstate 80 in northern Indiana. All samples were AC20 grade asphalt cement produced by Ashland Asphalt, supplied by the Louisville terminal, and purchased by Gohmann Asphalt. These samples generated chromatograms with nearly identical shape, as shown in Figure 4-2. The calculated fractional sizes also indicated that the samples exhibited nearly identical curve values, as shown in Table 4-1, and in Figure 4-3. These results demonstrated that the HPGPC system used for this study could produce nearly identical results for asphalts from one source with little effect on the chromatogram due to original asphalt age.

Calibration of the HPGPC system consisted of injecting eight commercially prepared polystyrene samples and

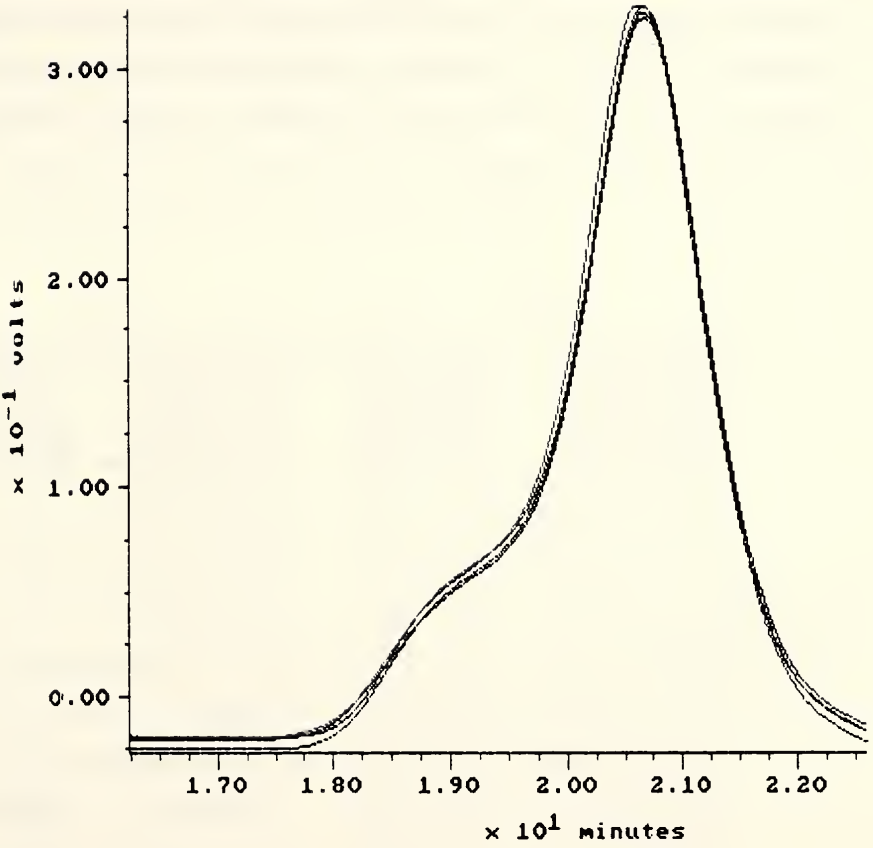

Figure 4-2. Overlay of Asphalt Samples from One Supplier and Plant

Table 4-1. Fractional Sizes of Asphalt Samples from One Supplier and Plant

	Sample:	I80-1	I80-2	I80-3	I80-4
Parameter	Date:	5/17	5/24	6/1	6/7
LMS		11.63	12.32	12.03	12.19
MMS		64.84	66.18	65.17	65.00
SMS		23.53	21.50	22.80	22.81

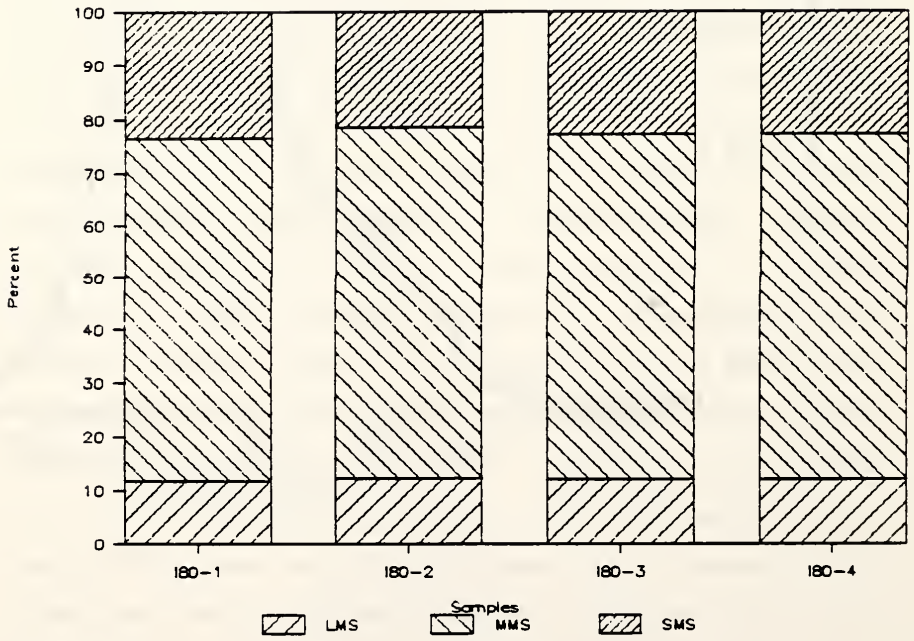

Figure 4-3. Fractional Sizes of Asphalt Samples from One Supplier and Plant

measuring the response of their elution from the column. Each sample consisted of a carefully measured narrow band of molecule weights. Samples were prepared for injection as described in Section 3.1.2, and their chromatograms were measured. The elution times were plotted versus molecular weights, and regression analysis was used to develop a calibration curve and regression equation for the system. A sample calibration curve is presented in Figure 4-4. The regression equation for this curve is:

$$\log Mw = 16.4605 - 2.8118R + 2.9599R^2 - .015150R^3$$

where, Mw = molecular weight

R = Retention time, (minutes x 10)

This equation has an r^2 value of .998025.

Calibration was performed each week that chromatographic analysis was conducted. The calibration curve for that particular week was then used to perform the area calculations of all chromatograms run on samples during that week.

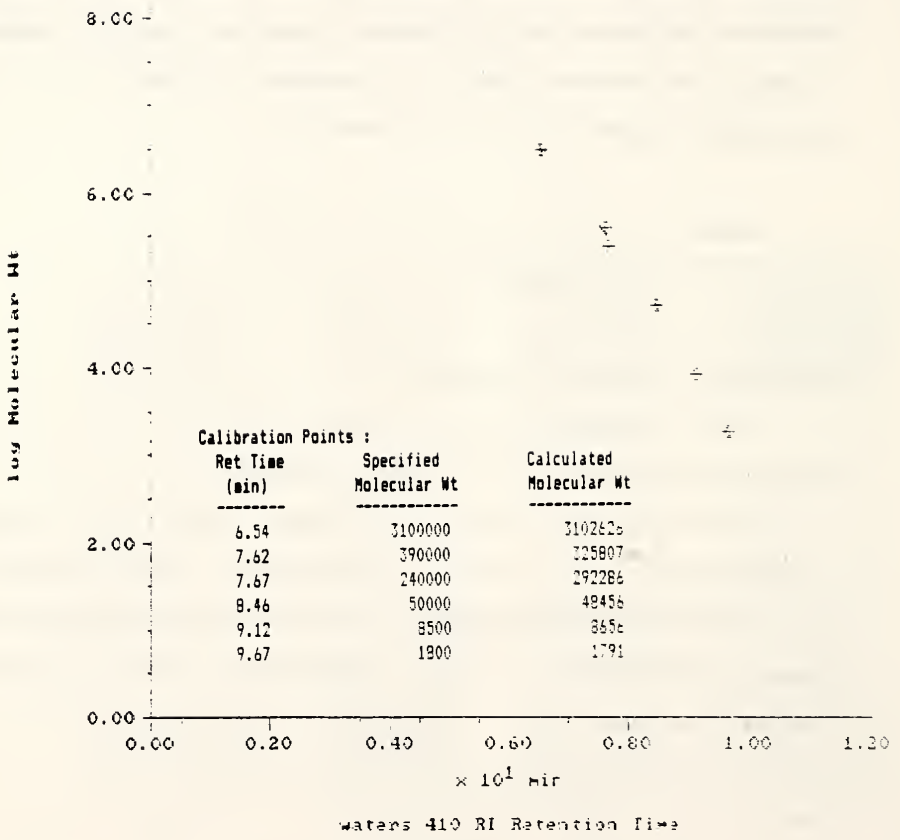

Figure 4-4. Calibration Curve for HPGPC System

The analysis of chromatograms consisted of calculation of several parameters that described the curve representing molecular size distribution. These parameters included percentages of large, medium and small molecular sizes, molecular averages, and measures of the curve broadening.

The percentages of molecular sizes were determined by dividing the area under the curve into three equal-time divisions. This first involved enlarging the chromatogram to ascertain the points of departure and return to baseline. Any variation in selection of the start and end point of the curve affects the percentages and molecular size calculations. After start and end points were determined, a unit of time that would enable the curve to be divided into thirds was selected. A time interval of five seconds was selected to enable this division and to be sufficiently short to enable accurate area calculations. The curve was then divided into five second slices by the computer, with the printout presenting slice mid-point, corresponding molecular weight, slice height, slice area and cumulative area percentage. An example of this printout is shown in Figure 4-5, with LMS, MMS, and SMS percentages highlighted. Slice mid-points, molecular sizes and slice divisions were also indicated on the chromatograms, as shown in Figure 4-6.

MAXIMA (c) 1987 Dynamic Solutions Division of Millipore

MAXIMA 820 GPC ANALYSIS REPORT

Printed: 16-JUL-1990 9:19:14

SAMPLE: af4orig
Type : UNKN
81 in Method : ASPHALT HP-GPC
Instrument : Instrument 1
Acquired : 8-MAY-1990 15:25
Filename : af4orig
Rate : 2.000 points/sec
Index : Disk
Duration : 15.000 minutes
Injection Volume : 100.000
Operator : tbn

ANALYSIS PARAMETERS:
Processing Start : 8.17 minutes
Baseline Start : 5.00 minutes
Processing End : 11.17 minutes
Baseline End : 14.00 minutes
Number of Slices : 36
Slice Width : 5.00 seconds

DETECTOR: waters 410 RI

Molecular Weight Distribution Averages:
Number Average : 284
Polydispersity : 15.366313
Weight Average : 4357
Z avg / Wt avg : 4.507733
Z Average : 19639
Z+1 avg / Wt avg : 8.708725
Z+1 Average : 37942

Peak Maximum:
Slice # : 18
Molecular Wt : 2035

Slice Detail:

	Slice #	Ret Time (minutes)	Molecular Wt	Slice Height (microvolts)	Slice Area (microvolt-sec)	Cumulative Area Pcnt
	1	8.21	87930	4503	23548	0.05
	2	8.29	72279	13863	70572	0.18
	3	8.37	59261	28863	145420	0.46
	4	8.46	48456	49289	247004	0.94
	5	8.54	39509	72833	364516	1.65
LMS	6	8.62	32119	97572	488050	2.59
	7	8.71	26032	122304	611633	3.77
	8	8.79	21031	146788	734209	5.20
	9	8.87	16934	172165	861318	6.86
	10	8.96	13589	200585	1003841	8.80
	11	9.04	10866	235303	1178287	11.08
	12	9.12	8656	280445	1405850	13.80
	13	9.21	6870	342253	1716198	17.13
	14	9.29	5431	425506	2132889	21.25
	15	9.38	4276	531048	2657871	26.40
	16	9.46	3353	646835	3231583	32.65
	17	9.54	2618	748068	3730287	39.87
MMS	18	9.63	2035	804872	4009620	47.63

Figure 4-5. Sample Printout of Chromatographic Data

	19	9.71	1575	800417	3990598	55.35
	20	9.79	1213	744515	3716994	62.54
	21	9.88	930	657584	3287768	68.90
	22	9.96	709	562653	2815802	74.35
	23	10.04	538	474856	2377043	78.95
	24	10.13	406	398688	1995757	82.81
SMS	25	10.21	305	334791	1674020	86.05
	26	10.29	228	276585	1384022	88.73
	27	10.38	170	226247	1133576	90.92
	28	10.46	125	186716	936601	92.73
	29	10.54	92	159069	796925	94.28
	30	10.63	67	137654	688592	95.61
	31	10.71	49	116537	581861	96.74
	32	10.79	35	92664	463445	97.63
	33	10.88	25	71079	358065	98.32
	34	10.96	18	61050	306696	98.92
	35	11.04	13	58086	290018	99.48
	36	11.13	9	53887	269030	100.00
	TOTAL				51679508	

Figure 4-5. Continued

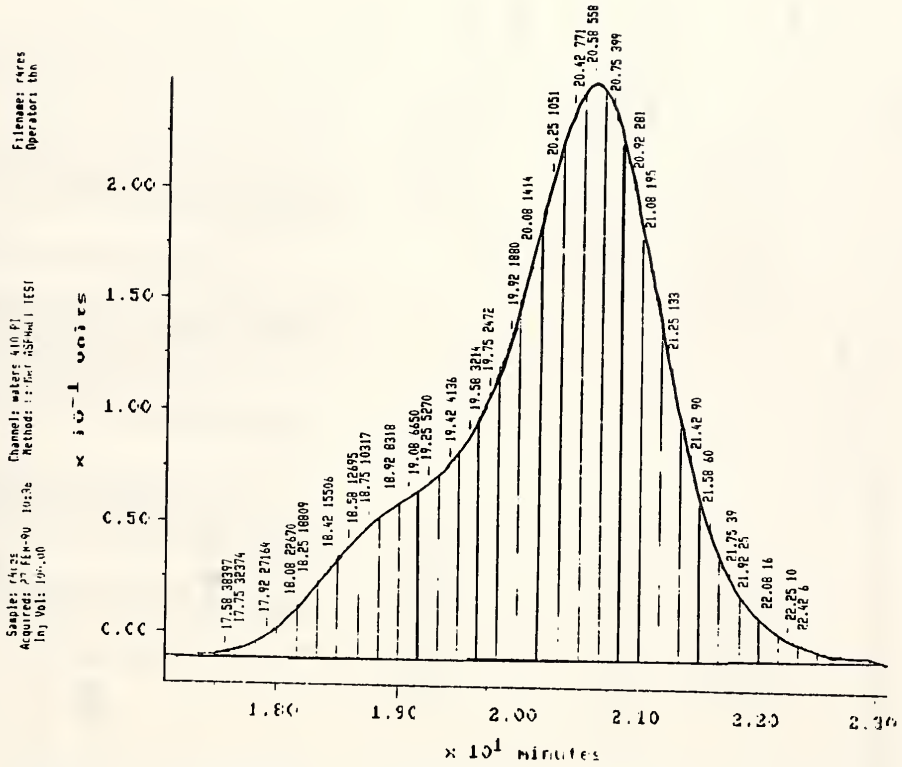

Figure 4-6. Printout of Chromatogram Showing Slices and Molecular Weights

The chromatogram curve parameters that were calculated for this study were measures of molecular averages and the range of molecular weights. The molecular averages included both number average molecular weight (Mn), and weight average molecular weight (Mw). These are defined as follows: [26]

$$Mn = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{\Sigma W_i}{\Sigma (W_i/M_i)}$$

$$Mw = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \frac{\Sigma W_i M_i}{\Sigma W_i}$$

where, N_i = number of molecules of molecular weight, Mi

W_i = weight of molecules of molecular weight Mi.

The ratio of Mw/Mn, defined as polydispersity, is a measure of the breadth of the chromatogram, and was also calculated. Values of polydispersity range from 1.0 for a very narrow spiked curve representing a sample in which all molecules are identical, to values of over one hundred for long, flat curves, Larger values indicate more complexly cross-linked polymers [26]. Typical polymers have polydispersity values that range from 2 to 5.

Additional parameters calculated included the z-average molecular weight and the z+1-average molecular weight, defined as follows:

$$Mz = \frac{\Sigma N_i M_i^3}{\Sigma N_i M_i^2}$$

and

$$Mz+1 = \frac{\Sigma N_i M_i^4}{\Sigma N_i M_i^3}$$

where N_i, M_i and W_i have the same definitions as stated earlier.

These values have been used in analyses of polymers [26] to indicate flexibility or stiffness of polymers. These parameters were also normalized by dividing by the weight-average molecular weight (Mw). In addition to the fact that these parameters have been used in polymer analysis, additional support for their inclusion in asphalt analysis is seen by the location of these parameters in a plot of a chromatogram of asphalt. The z-average and z+1 average molecular weight values lie in the higher molecular size area of the curve, which represents the larger molecule size, area of the curve. This is shown in Figure 4-7.

It is expected that any change in the lower molecular size portion of the curve will greatly affect the Mn value, but have little effect on the Mz or Mz+1 values. Conversely, a change in the high molecular weight fraction will affect the latter parameters, while having little effect on the former. Since the higher molecular weight region of the curve represents asphaltenes (or an agglomeration of molecules that approximates asphaltenes), the Mz and Mz+1 parameters should be analyzed.

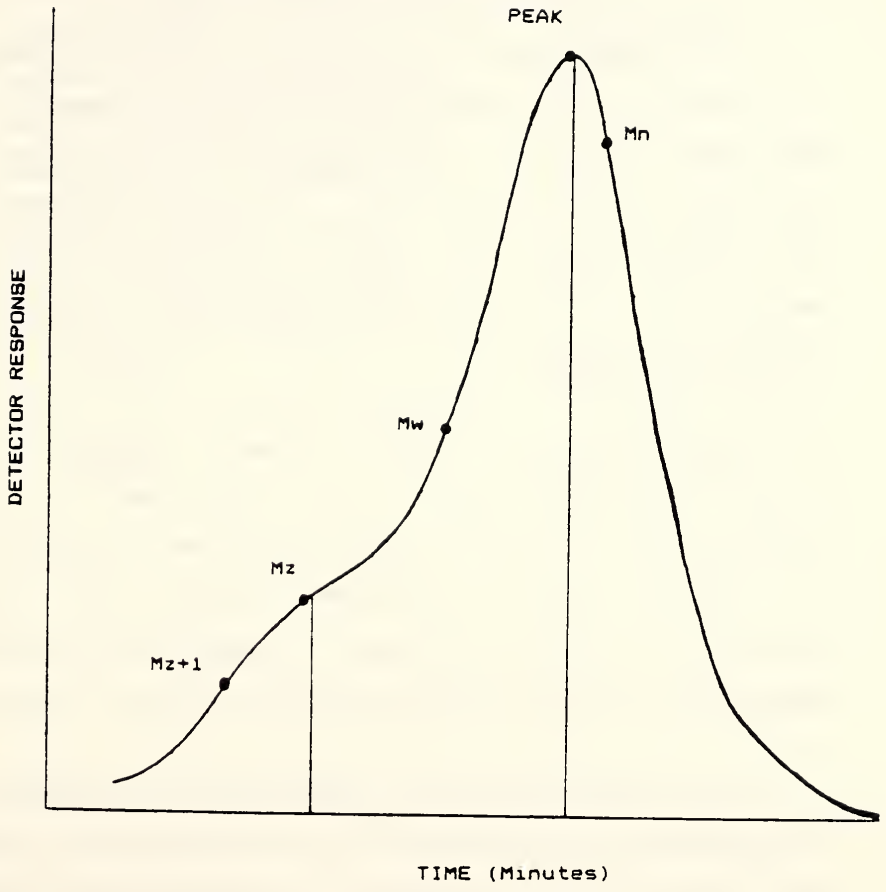

Figure 4-7. Relationship of Parameters to Chromatogram

A summary of the parameters used to analyze the chromatograms is presented in Table 4-2.

4.2 - Statistical Analysis

4.2.1 - Tests on Original Asphalt

The original asphalt was analyzed to determine whether any correlation was evident between physical properties of the asphalt cement and the chromatographic parameters of the asphalt used in this study. This was accomplished by first plotting each of the physical properties versus the chromatogram parameters, and then using statistical analysis to determine the strength of the correlations between parameters.

Each of the nine measured physical parameters was plotted against each of ten parameters of the chromatographs for the 16 original asphalts using Lotus 1-2-3 software and its Printgraph function [66]. This resulted in a total of 90 graphs. A summary of the plotted parameters and the abbreviations used are given in Table 4-3.

Each of the nine physical properties was then analyzed for possible correlations with the ten chromatogram values. This analysis was performed by determining Pearson Correlation Coefficients (r). Pearson coefficients indicate how closely two parameters are correlated in a linear relationship [67]. The equation used to determine r values is:

Table 4-2. Chromatogram Parameters Measured

Parameter	Abbreviation(s)
Number Average Molecular Weight	Mn
Weight Average Molecular Weight	Mw
Polydispersity	POLY;(Mn/Mw)
Large Molecular Size Fraction	LMS
Medium Molecular Size Fraction	MMS
Small Molecular Size Fraction	SMS
Z-average Molecular Weight	Mz
z+1 average Molecular Weight	Mz+1
Normalized Z-average molecular Weight	MzRAT; (Mz/Mw)
Normalized z+1 average Molecular Weight	Mz+1RAT; (Mz+1/Mw)

Table 4.3. Parameters of Original Asphalts Used in Analysis

Physical Measures

Parameter	Abbreviation
Penetration	PEN
Kinematic Viscosity	KVIS
Absolute Viscosity	AVIS
Specific Gravity	SPGR
Penetration Visc. Number	PVN
Visc. Temp. Susceptibility	VTS
Penetration Retained (TFOT)	PENRET
Absolute Visc. Ratio (TFOT)	AVISRAT
Kinematic Visc. Ratio (TFOT)	KVISRAT

Chromatogram Measures

Parameter	Abbreviation
Large Mole. Size	LMS
Medium Mole. Size	MMS
Small Mole. Size	SMS
Number Ave. Mole. Weight	Mn
Weight Ave. Mole. Weight	Mw
Polydispersity (Mn/Mw)	POLY
Z-average Mole. Weight	MZ
Z+1-average Mole. Weight	MZ + 1
Ratio of Mz/Mw	MZRAT
Ratio of Mz+1/Mw	MZ+1RAT

$$r = \frac{N\Sigma xy - (\Sigma x)(\Sigma y)}{\sqrt{N\Sigma x^2 - (\Sigma x)^2} * \sqrt{N\Sigma y^2 - (\Sigma y)^2}}$$

Values of r near zero indicate little or no linear relationship between variables. Values of r close to 1 or -1 indicate strong positive or negative relationships [68]. The physical parameter was used as the dependent variable, and the ten chromatogram values were the independent variables against which physical parameters were compared. Pearson correlations were run for each of the nine physical properties, using the same ten chromatogram variables for each run.

4.2.2 - Tests on Asphalt Aging

Asphalt samples were analyzed to determine whether HPGPC techniques could detect changes in asphalt due to age hardening. Additionally, objectives of this project were to determine whether differences could be detected between asphalt mixes produced by batch plants and drum mix plants, and by plants using different burner fuels. These objectives could be investigated by performing an analysis of variance (ANOVA) of the values obtained for the asphalts at each stage of age hardening. Both physical properties and chromatograms were evaluated, in order to determine whether HPGPC techniques were more sensitive to changes than the more traditional physical tests of asphalt properties.

The model used to test the hypothesis that the means of the values at each stage are not equal was:

$$Y = u + S_i + P_j + F_k + SP_{ij} + SF_{ik} + FP_{jk} + SFP_{ijk} + e_{ijkl}$$

where, S = effects of stage of aging

P = effects of plant type (drum or batch)

F = effect of fuel used to dry aggregate

i=1,2,3,4 j=1,2 k=1,2,3,4

l=2 (two samples of each combination)

The main effects of stage, plant and fuel type were of primary interest. ANOVA evaluation was performed for each variable considered in this study. This resulted in ten runs for physical properties and ten runs for chromatographic parameters. This evaluation would not only indicate whether effects were significant, but also which parameter, if any, (either physical or chromatographic) was most sensitive to detecting these effects.

A diagram of the organization of samples for ANOVA evaluation is provided as Figure 4-8.

Stage(S)	Plant Type (P)							
	Drum				Batch			
	Fuel (F)				Fuel (F)			
	G	R	T	F	G	R	T	F
Orig.	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
TFOT	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
Mix	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
Core	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-

Figure 4-8. Organization of Samples for Aging Study

4.2.3 - Tests on Fuel Contamination

Analysis of variance was also used to evaluate whether fuel contamination could be detected by either tests of physical properties, the resulting mixes, or by HPGPC techniques. The hypothesis that the means (for physical properties or chromatographic values) are not equal was evaluated using the model:

$$Y = u + C_i + F_j + CF_{ij} + e_{ij}k$$

where, C = condition (contaminated or not contaminated)

F = fuel used

i = 1,2

j = 1,2,3 (No. 2, No. 4 burner fuels, Gas)

k = 1,2 (for 2 samples of each combination)

Condition was the main effect of major interest in this portion of the study. Interaction of condition and fuel was of nearly equal interest. The main effect of fuel type was evaluated in more detail in the study of asphalt aging.

ANOVA evaluation was used to rate the samples. The physical parameters of penetration, absolute viscosity, kinematic viscosity, penetration-viscosity number, and viscosity-temperature susceptibility were established. The chromatographic values of LMS, MMS, SMS, Mw, Mn and polydispersity were used for the analysis. In addition,

mixes prepared with uncontaminated and contaminated asphalt cements were tested for Indirect Tensile Strength, Marshall Stability and Marshall Flow. This required five evaluations for physical parameters, three evaluations of mix strength properties, and six evaluations for chromatographic parameters to determine which, if any, of the parameters could be used to detect fuel contamination. An evaluation of which types of fuel contamination could be detected was also of interest in this portion of the study.

CHAPTER 5

RESULTS: TESTS ON ORIGINAL ASPHALTS

This chapter presents the results of tests of the physical parameters and high pressure gel permeation chromatography (HPGPC) of the asphalt samples. The first section details the asphalt parameters and calculated indices and the second section presents results of analysis by HPGPC techniques. The final section compares HPGPC results to physical properties.

5.1. - Physical Parameters of Tested Asphalts

Physical parameters of the sixteen asphalt samples tested are presented in Table 5-1. The parameters measured include penetration (77°F), viscosity at 140°F (Absolute Viscosity), viscosity at 275°F (Kinematic Viscosity), and specific gravity. All measured physical parameters meet the minimum Indiana requirements for AC-20 asphalt. In addition to the measured physical parameters, temperature susceptibility values for penetration-viscosity number (PVN), viscosity temperature susceptibility (VTS) were calculated. The values for temperature susceptibility are given in Table 5-2. Figures 5-1 through 5-6 show plots of the physical parameters and temperature-susceptibility values for original asphalts.

Table 5-1. Physical Parameters of Asphalts

Sample	Pen	Kin Visc (135°C)	Abs Visc (60°C)	Sp Grav
G1	67	418.2	2395.7	1.0275
G2	68	328.1	2554.9	1.0255
G3	57	374.9	2273.6	1.0258
G4	78	384.2	2070.1	1.0264
R1	75	415.1	2417.9	1.0258
R2	58	374.9	2206.4	1.0398
R3	71	407.1	2993.6	1.0253
R4	74	426.5	2170.1	1.0247
T1	54	361.3	2377.5	1.0222
T2	72	405.8	2199.8	1.0264
T3	50	404.1	2428.8	1.0237
T4	64	408.5	3050.6	1.0234
F1	63	305.9	3511.6	1.0332
F2	56	363.6	3079.7	1.0143
F3	64	386.9	2348.3	1.0262
F4	52	311.9	2791.4	1.0369

Table 5-2. Temperature Susceptibility Values for Original Asphalts

Sample	PVN	VTS
G1	-0.60	1.29
G2	-0.93	1.54
G3	-0.91	1.35
G4	-0.56	1.27
R1	-0.49	1.30
R2	-0.90	1.33
R3	-0.58	1.45
R4	-0.47	1.21
T1	-1.01	1.41
T2	-0.57	1.26
T3	-0.93	1.33
T4	-0.68	1.46
F1	-1.10	1.79
F2	-0.97	1.57
F3	-0.76	1.34
F4	-1.25	1.64

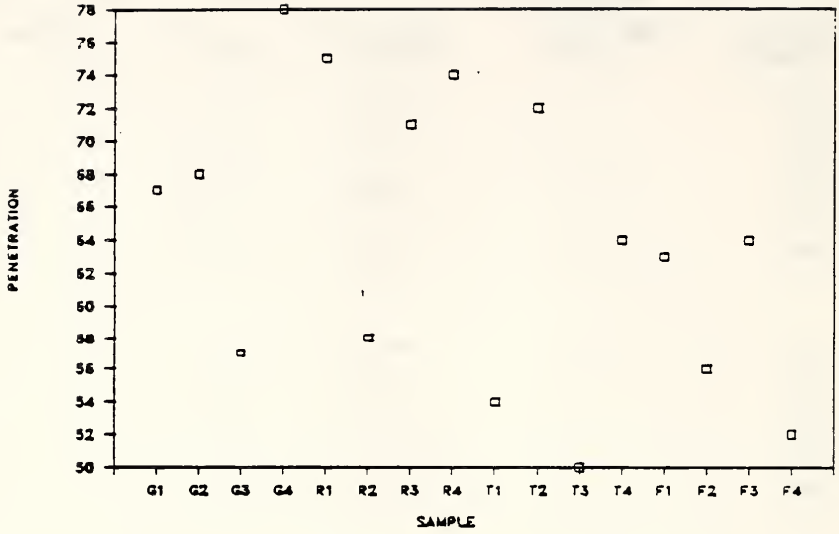

Figure 5-1. Penetration Values for Original Asphalt

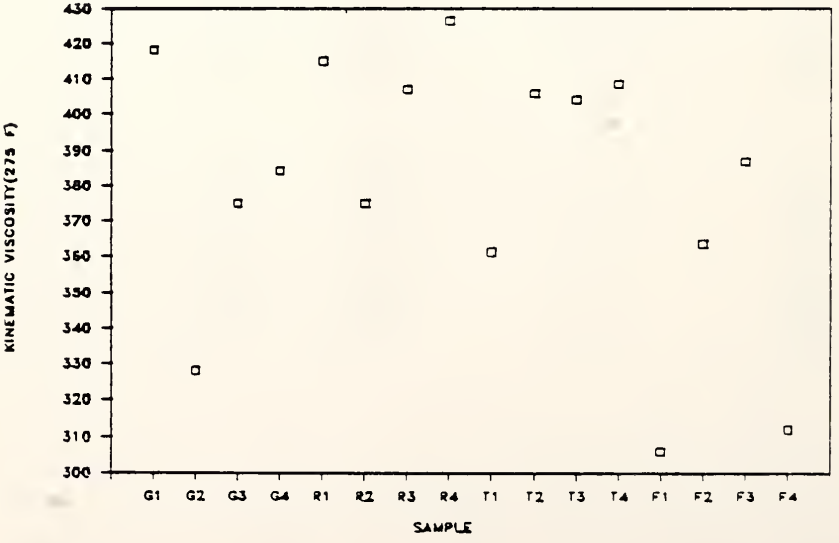

Figure 5-2. Kinematic Viscosity Values for Original Asphalt

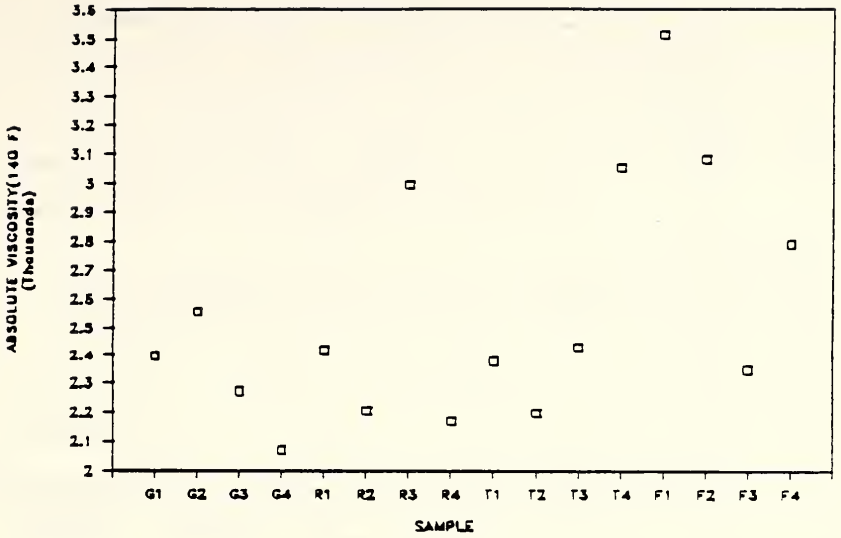

Figure 5-3. Absolute Viscosity Values for Original Asphalt

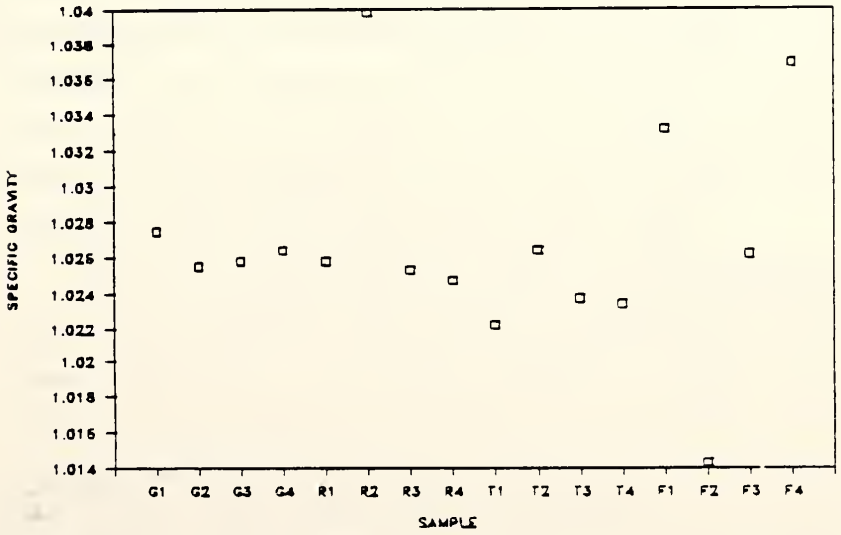

Figure 5-4. Specific Gravity Values for Original Asphalt

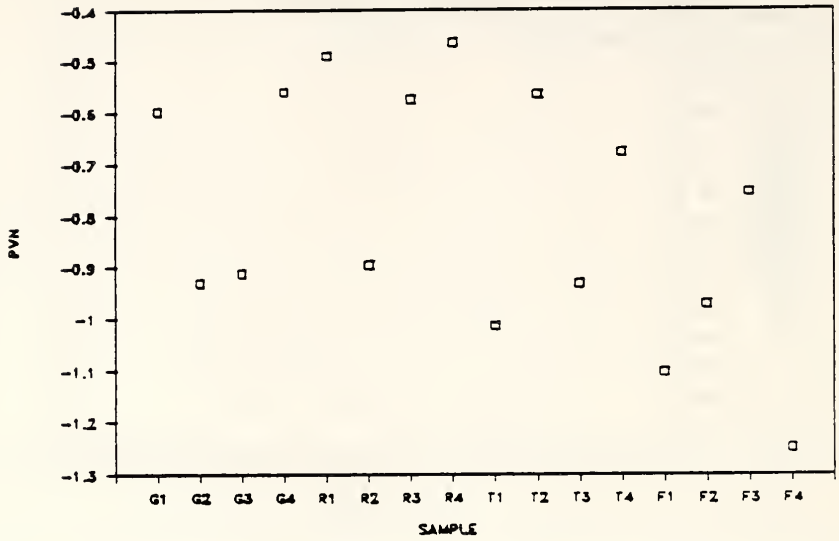

Figure 5-5. Penetration-Viscosity Numbers for Original Asphalt

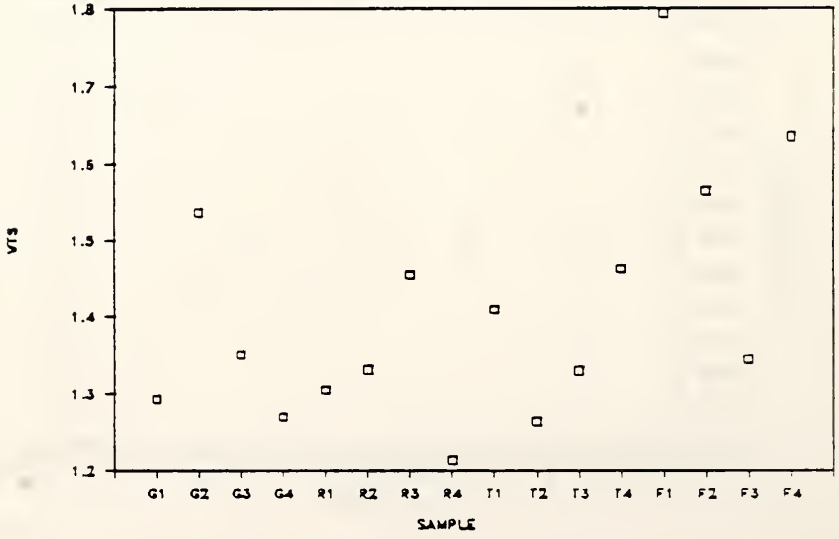

Figure 5-6. Viscosity-Temperature Susceptibility Values for Original Asphalt

Measures of age hardening of the asphalt samples were also determined after exposure of the original asphalts to the thin film oven test. The age hardening measures of penetration retained, viscosity ratio (140°F) and viscosity ratio (275°F) are provided in Table 5-3.

5.2 - Chromatographic Analysis of Original Asphalts

Chromatograms for each of the sixteen original asphalt samples were obtained and saved to form a data base of Indiana asphalts. Figure 5-7 shows a typical curve for one of the original samples (F3). All of the original asphalts produced chromatograms with the same general shape, having a single peak at an elution time of approximately twenty minutes or ten minutes, depending upon the flow rate of the pump. The two flow rates resulted when the pump was serviced during the testing period, producing a more efficient flow rate than originally achieved at the same pump setting. All samples within a test or group of samples being compared were run at the same flow rate in order to ensure that comparisons could be made.

Table 5-4 presents the LMS, MMS, and SMS fractions for the original asphalts, and Figure 5-8 graphically depicts these fractions. As can be seen by the data, the LMS fraction varies the least, with a mean value of 11.76% and standard deviation of 1.54 and a coefficient of variability of 13.16%. The lighter ends, represented by SMS and MMS fractions show greater variation among the asphalt samples.

Table 5-3. Age Hardening Parameters of Original Asphalt

Sample	Pen Retained (%)	Visc. Ratio (140°F)	Visc. Ratio (275°F)
G1	56.7	1.85	2.99
G2	58.8	1.75	2.31
G3	64.9	1.45	1.87
G4	59.0	1.72	4.04
R1	62.7	1.49	2.83
R2	63.8	1.44	2.85
R3	59.2	1.93	2.67
R4	62.2	1.41	2.41
T1	68.5	1.69	2.93
T2	65.3	1.47	2.88
T3	68.0	1.34	2.45
T4	67.2	1.48	3.08
F1	61.9	1.86	1.54
F2	61.1	1.44	1.81
F3	62.5	1.59	2.47
F4	69.2	1.63	1.58

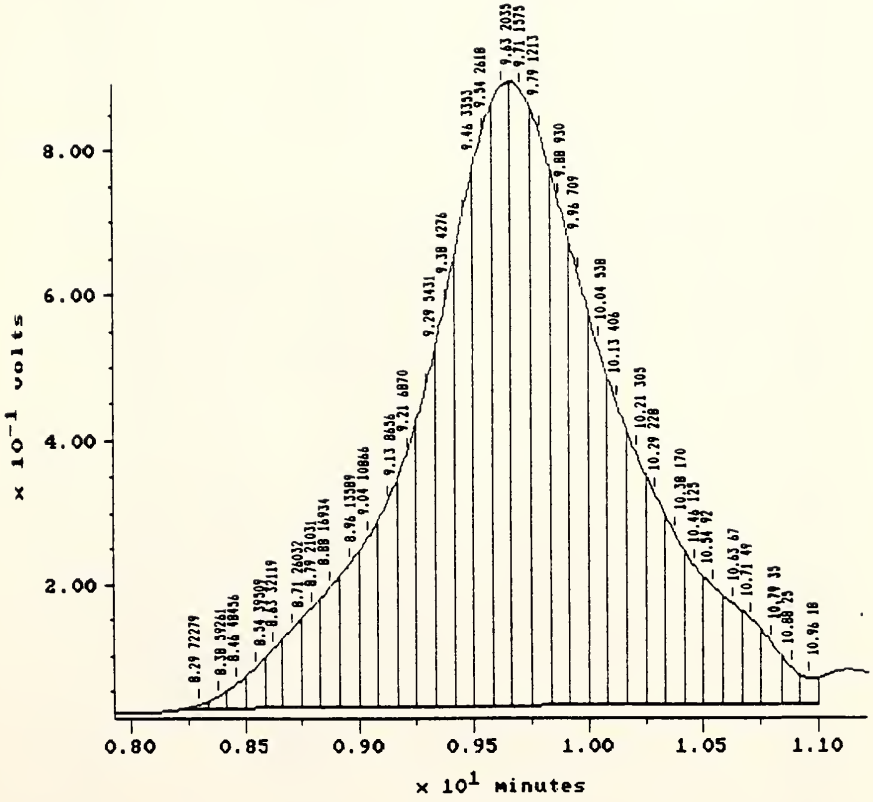

Figure 5-7. Chromatogram of Original Asphalt Sample

Table 5-4. Molecular Size Fractions for Original Asphalts

Sample	LMS	MMS	SMS
G1	11.14	58.83	30.03
G2	12.33	56.47	31.2
G3	10.64	58.68	30.68
G4	11.92	59.78	28.3
R1	12.78	56.14	31.08
R2	9.89	57.84	32.27
R3	11.89	59.66	28.45
R4	11.39	59.51	29.1
T1	14.41	67.26	18.33
T2	10.56	39.32	50.12
T3	8.56	42.19	49.25
T4	12.65	68.02	19.33
F1	12.3	58.33	29.37
F2	12.83	63.38	23.79
F3	10.51	54.83	34.66
F4	14.36	64.86	20.78
Mean:	11.76	57.82	30.42
SD:	1.54	7.68	8.88
CV:	13.16	13.29	29.19

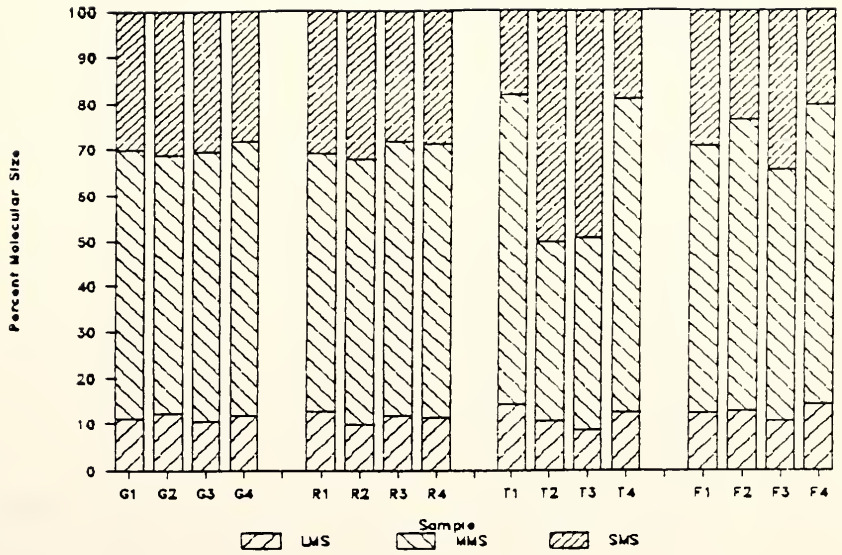

Figure 5-8. Distribution of Molecular Sizes for Original Asphalt

Chromatogram molecular weight parameters for each of the original samples are presented in Table 5-5. Plots of these values are presented in Figures 5-9 through 5-15. These plots show that all of the chromatographic parameters vary considerably, although less than molecular sizes, with coefficients of variation ranging from 6.4% to 16.5%.

5.3 - Comparison of Physical Parameters and Chromatograms

Each of the physical parameters was compared to the chromatograph parameters. Plots of the relationships are included in the data base. Pearson Correlation coefficients, indicating the strength of the relationships, are discussed in Section 8.2.

Table 5-5. Chromatogram Parameters for Original Asphalts

Sample	Mw	Mn	Polydis	Mz	Mz/Mw	Mz+1
G1	3500	520	6.727464	12543	3.584034	20899
G2	3741	487	7.679219	13679	3.656414	22419
G3	3393	515	6.588643	12345	3.63833	20963
G4	3750	549	6.835753	14116	3.764165	23429
R1	3219	508	6.337887	11086	3.443413	18159
R2	4076	590	6.90656	14967	3.672365	26311
R3	3811	560	6.80822	14728	3.84746	25070
R4	3593	559	6.425813	13143	3.658257	21864
T1	3045	605	5.030457	9405	3.088936	15617
T2	3338	522	6.393953	11876	3.55816	19527
T3	3016	578	5.215136	10483	3.475466	18964
T4	2628	396	6.640504	9458	3.599146	15970
F1	3883	547	7.094062	15120	3.893404	25550
F2	3362	680	4.946539	10548	3.137204	17635
F3	3685	533	6.915711	13837	3.75551	23616
F4	3016	545	5.530835	10101	3.348575	16944
Mean:	3441	543.4	6.3798	12339.7	3.5700	20806.6
SD:	387.7	60.3	0.789	1976.3	0.228	3433.6
CV:	11.27	11.09	12.37	16.02	6.38	16.50

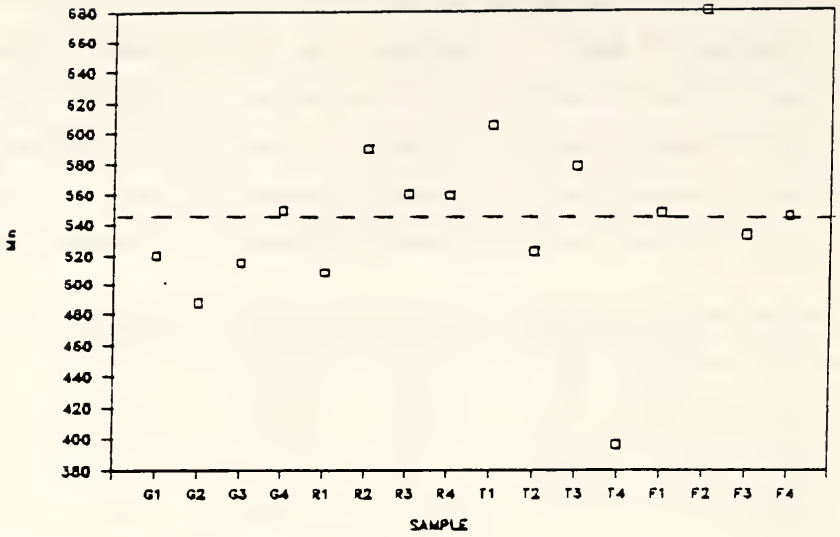

Figure 5-9. Mn Values for Original Asphalts

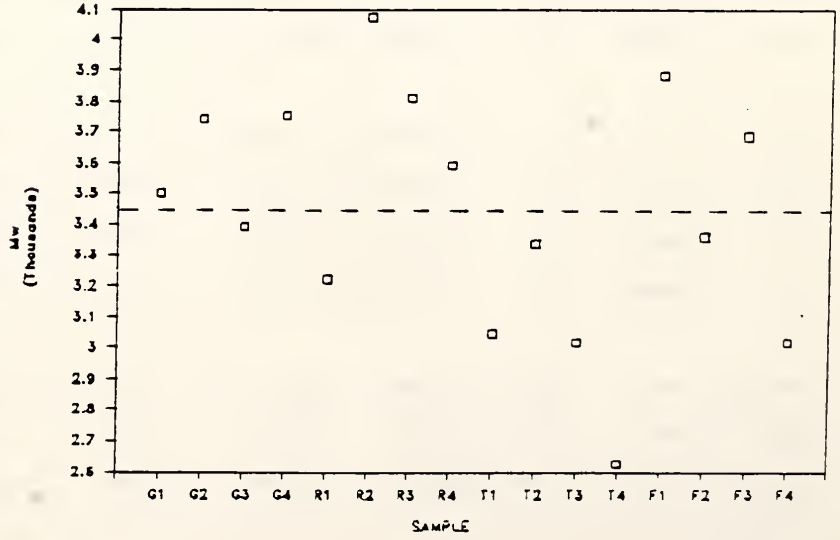

Figure 5-10. Mw Values for Original Asphalts

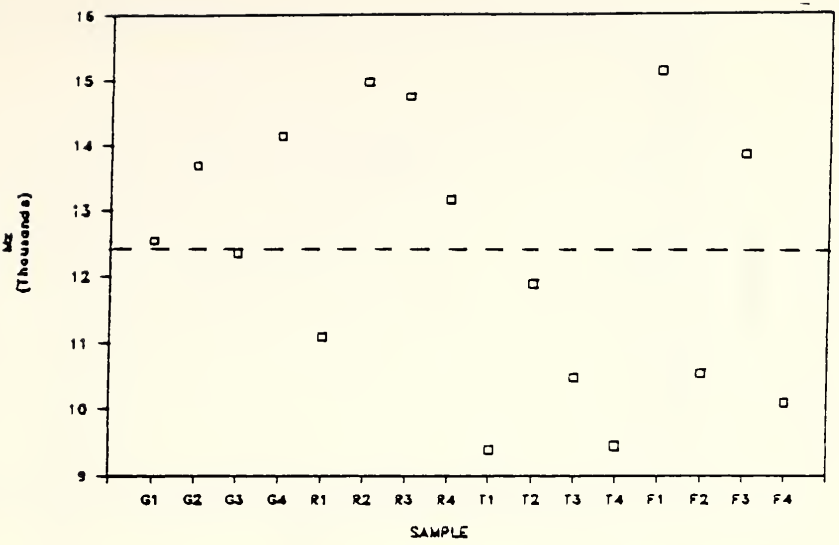

Figure 5-11. Mz Values for Original Asphalts

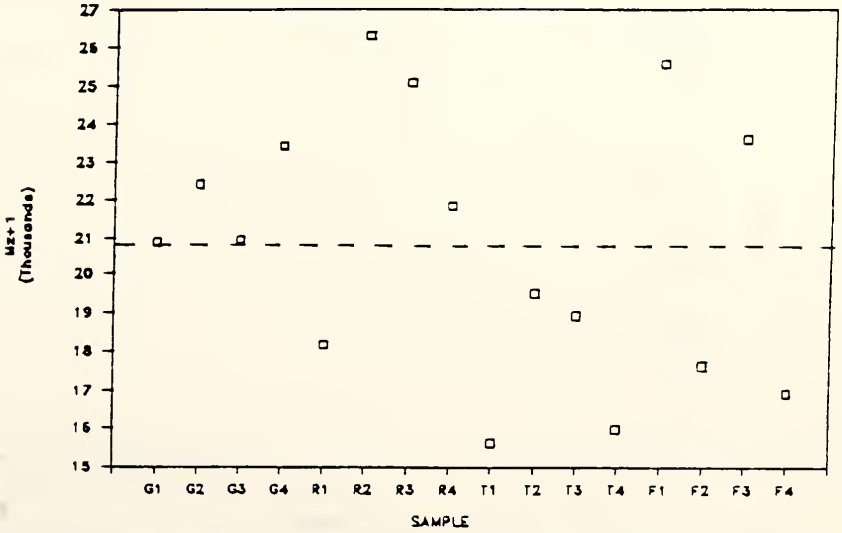

Figure 5-12. Mz+1 Values for Original Asphalts

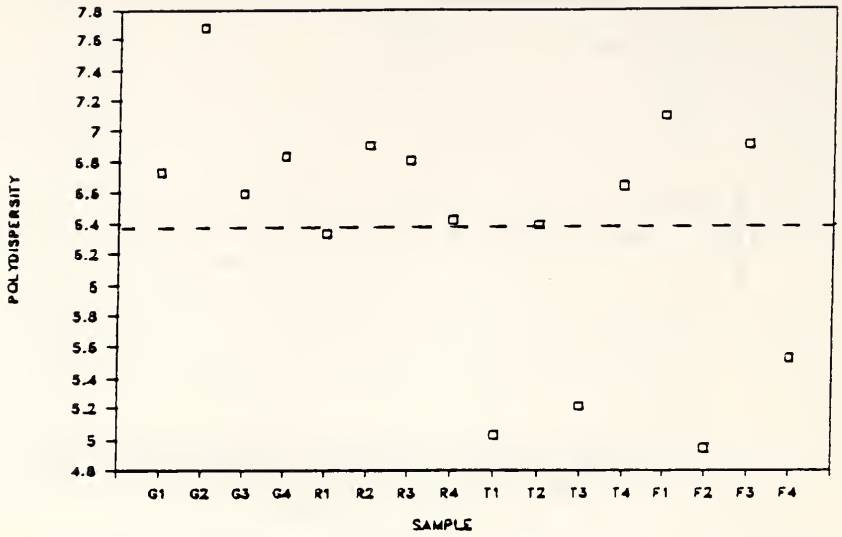

Figure 5-13. Polydispersity Values for Original Asphalts

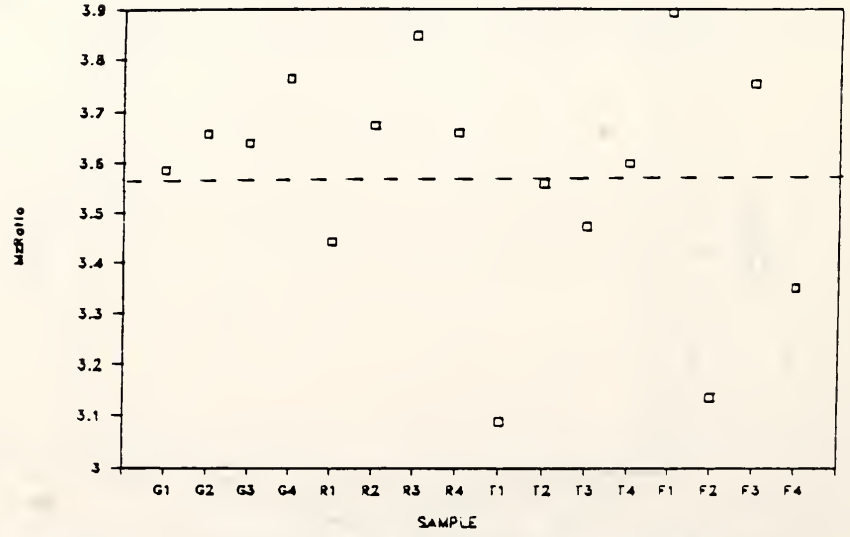

Figure 5-14. Mz/Mw Values for Original Asphalts

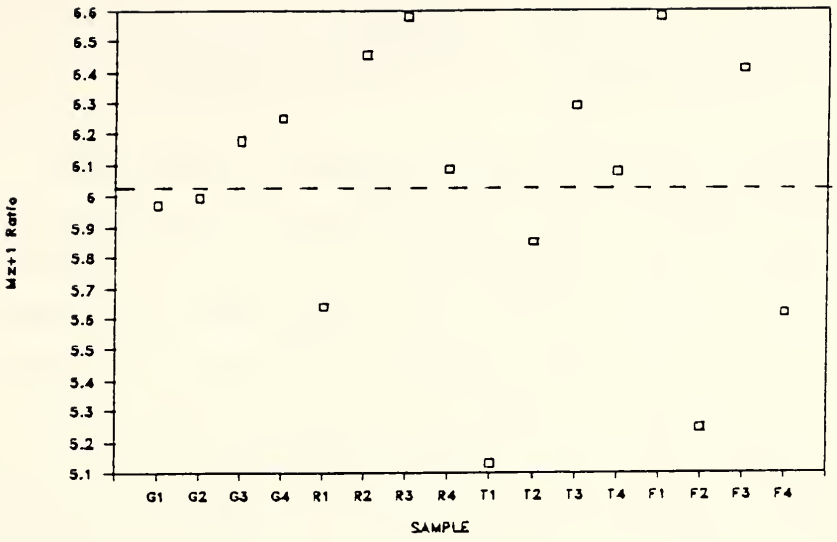

Figure 5-15. Mz+1/Mw Values for Original Asphalts

CHAPTER 6

RESULTS: TESTS ON AGING OF ASPHALT

This chapter presents the results of tests to measure the physical parameters and the chromatographic characteristics of aged asphalt cements. Three stages of asphalt aging were evaluated. Aging was measured after processing in hot mix asphalt plants, after exposure to the thin film oven test (TFOT), and after five years of service in an asphaltic concrete pavement. The first section of this chapter presents the results of tests of the changes in physical parameters of the asphalt. The second section presents results of chromatographic evaluation of the asphalts.

6.1 - Physical Changes in Aged Asphalt

The asphalt aging stages that were evaluated were: the baseline of original asphalt; asphalt after Thin Film Oven Testing; asphalt after processing in both drum mix and batch type asphalt plants; and asphalt after five years of service in a flexible pavement. Original asphalt was used for the thin film oven test, while asphalt samples were extracted from the mix and recovered cores for the mix and five year aging samples, respectively.

Each asphalt was tested for penetration at 77°F, absolute viscosity (140°F), and kinematic viscosity (275°F). Temperature susceptibility indices of penetration-viscosity number (PVN), viscosity-temperature susceptibility (VTS) and penetration index (PI) were then calculated from these values. The results of the testing for the original asphalt are given in Table 6-1. These are the same results reported in Chapter 5, since they were applied to both studies.

Table 6-2 shows the results of the tests on the thin film oven test samples after 5 hours exposure. In addition to the measures of penetration and viscosity used for comparison with original asphalt, TFOT samples were also measured for penetration retained, and viscosity ratios at 140°F and 275°F. These values are included in Table 6-3.

Asphalt samples extracted from the mixes that were produced using the original asphalt were also evaluated for penetration, absolute viscosity (140°F) and kinematic viscosity (235°F). These results are given in Table 6-4, along with the calculated values of PVN and VTS. Penetration retained values and viscosity ratios (compared to the original asphalt) were also calculated for use in evaluating how well the thin film oven test approximates the aging produced in asphalt plants. These values are shown in Table 6-5.

Table 6-1. Physical Parameters of Original Asphalts

Sample	Pen	AVis	KVis	PVN	VTS
G1	67	2395.7	418.2	-0.60	1.29
G2	68	2554.9	328.1	-0.93	1.54
G3	57	2273.6	374.9	-0.91	1.35
G4	78	2070.1	384.2	-0.56	1.27
R1	75	2417.9	415.1	-0.49	1.30
R2	58	2206.4	374.9	-0.90	1.33
R3	71	2993.6	407.1	-0.58	1.45
R4	74	2170.1	426.5	-0.47	1.21
T1	54	2377.5	361.3	-1.01	1.41
T2	72	2199.8	405.8	-0.57	1.26
T3	50	2428.8	404.1	-0.93	1.33
T4	64	3050.6	408.5	-0.68	1.46
F1	63	3511.6	305.9	-1.10	1.79
F2	56	3079.7	363.6	-0.97	1.57
F3	64	2348.3	386.9	-0.76	1.34
F4	52	2791.4	311.9	-1.25	1.64

Table 6-2 Physical Parameters of TFOT Aged Asphalts

Sample	Pen	Kvis	AVis
G1	38	775.1	7163.4
G2	40	574.6	5909.7
G3	37	543.6	4241.5
G4	46	661.6	8373.2
R1	47	618.1	6831.4
R2	37	538.8	6279.9
R3	42	787.6	7987.3
R4	46	602.8	5230.3
T1	37	611.2	6967.8
T2	47	596.5	6339.2
T3	34	541.7	5941.9
T4	43	602.8	9393.1
F1	39	568	5408.2
F2	51	524	5577.5
F3	40	613.6	5794.3
F4	36	509.7	4400.1

Table 6-3 Asphalt Aging Measures for Asphalt Aged in TFOT

Sample	Visc Rat 140°F	Visc Rat 275°F	Pen Ret
G1	1.85	2.99	0.57
G2	1.75	2.31	0.59
G3	1.45	1.87	0.65
G4	1.72	4.04	0.59
R1	1.49	2.83	0.63
R2	1.44	2.85	0.64
R3	1.93	2.67	0.59
R4	1.41	2.41	0.62
T1	1.69	2.93	0.69
T2	1.47	2.88	0.65
T3	1.34	2.45	0.68
T4	1.48	3.08	0.67
F1	1.86	1.54	0.62
F2	1.44	1.81	0.91
F3	1.59	2.47	0.63
F4	1.63	1.58	0.69

Table 6-4. Physical Parameters of Asphalt Extracted from Mixes

Sample	Pen	Kin Visc	Abs Visc	PVN	VTS
G1	56	523.8	5129.5	-0.47	1.57
G2	71	667.6	6084.2	0.14	1.48
G3	37	634.3	7507.4	-0.61	1.64
G4	62	665.2	4999.0	-0.02	1.37
R1	54	850.2	7875.0	0.16	1.44
R2	34	521.9	5870.7	-0.94	1.65
R3	42	801.6	10857.8	-0.18	1.66
R4	42	804.3	9790.4	-0.18	1.60
T1	48	520.5	4358.6	-0.63	1.48
T2	60	597.7	8189.3	-0.21	1.73
T3	34	633.4	10496.1	-0.69	1.82
T4	43	752.4	10846.0	-0.24	1.70
F1	54	428.6	4728.2	-0.78	1.68
F2	60	469.4	6179.1	-0.55	1.76
F3	49	1088.0	10797.3	0.39	1.43
F4	41	574.9	6665.3	-0.65	1.65

Table 6-5. Asphalt Aging Measures for Asphalt Extracted from Mixes

Sample	Pen Ret	Visc Rat(140°F)	Visc Rat(275°F)
G1	83.6%	1.25	2.14
G2	104.4%	2.03	2.38
G3	64.9%	1.69	3.30
G4	79.5%	1.73	2.41
R1	72.0%	2.05	3.26
R2	58.6%	1.39	2.66
R3	59.2%	1.97	3.63
R4	56.8%	1.89	4.51
T1	88.9%	1.44	1.83
T2	83.3%	1.47	3.72
T3	68.0%	1.57	4.32
T4	67.2%	1.84	3.56
F1	85.7%	1.40	1.35
F2	107.1%	1.29	2.01
F3	76.6%	2.81	4.60
F4	78.8%	1.84	2.39

Physical parameters of the asphalt extracted from the cores are given in Table 6-6. Information from the core asphalt samples was determined so that retained penetration and viscosity ratios could be used in the evaluation of the thin film oven test. The results of these calculations are provided in Table 6-7.

The effects of aging on the physical parameters of the asphalt are presented in Figures 6-1 through 6-5. These figures show that the measured physical parameters change in a consistent manner with increased aging. A more complete analysis of these changes is presented in the second section of Chapter 8, Discussion of Results.

6.2 - Chromatographic Changes in Aged Asphalt

Chromatograms of each of the sixteen different asphalts after TFOT, after mixing and after five years pavement life are included as an Appendix. Figure 6-6 shows a typical curve for a sample after TFOT. Figure 6-7 depicts the same asphalt sample after processing in an asphalt plant. Figure 6-8 shows the same asphalt extracted from a core taken from the pavement five years after processing and paving. The chromatographic parameters for the asphalts at each stage of aging are presented in Tables 6-8, 6-9, and 6-10, representing TFOT aging, asphalt plant aging and five years pavement aging respectively. The data for molecular size fractions is shown in a different format in Figures 6-9, 6-10 and 6-11, for TFOT, plant mix and cores, respectively.

Table 6-6. Physical Parameters of Asphalt Extracted from Cores

Sample	Pen	KVis	AVis	PVN	VTS
G1	13	1587.1	12704	-0.41	1.26
G2	9	2345.2	21907	-0.29	1.28
G3	15	1598.5	13673	-0.28	1.29
G4	15	1240.3	18979	-0.57	1.63
R1	11	1512.8	14222	-0.60	1.35
R2	18	1043.6	11129	-0.62	1.48
R3	12	1935.3	22135	-0.26	1.41
R4	12	1453.9	16960	-0.57	1.47
T1	23	899.4	14017	-0.58	1.71
T2	24	816.9	11123	-0.66	1.66
T3	16	1195.4	15149	-0.56	1.54
T4	21	868.2	11597	-0.70	1.63
F1	25	775.8	9781	-0.69	1.63
F2	17	894.9	14120	-0.84	1.71
F3	12	1552.8	17778	-0.50	1.45
F4	26	871.5	12153	-0.51	1.66

Table 6-7. Asphalt Aging Measures for Asphalt Extracted from Cores

Sample	Pen Ret	AVis Rat(140°F)	KVis Rat(275°F)
G1	19.4%	5.30	3.80
G2	13.2%	8.57	7.15
G3	26.3%	6.01	4.26
G4	19.2%	9.17	3.23
R1	14.7%	5.88	3.64
R2	31.0%	5.04	2.78
R3	16.9%	7.39	4.75
R4	16.2%	7.82	3.41
T1	42.6%	5.90	2.49
T2	33.3%	5.06	2.01
T3	32.0%	6.24	2.96
T4	32.8%	3.80	2.13
F1	39.7%	2.79	2.54
F2	30.4%	4.58	2.46
F3	18.8%	7.57	4.01
F4	50.0%	4.35	2.79

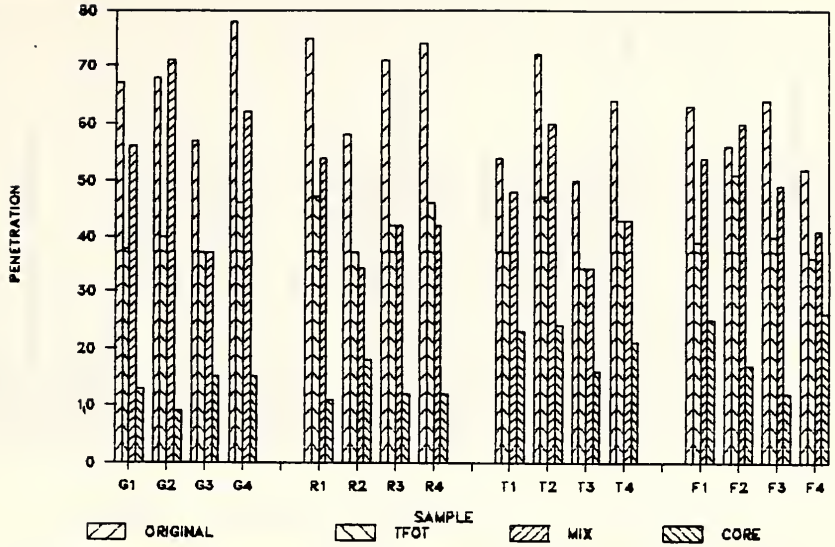

Figure 6-1. Changes in Penetration with Aging

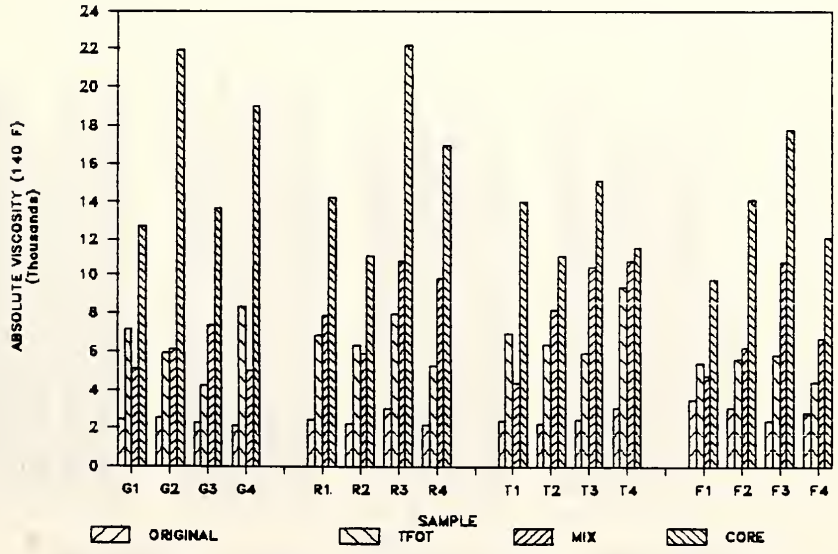

Figure 6-2. Changes in Absolute Viscosity with Aging

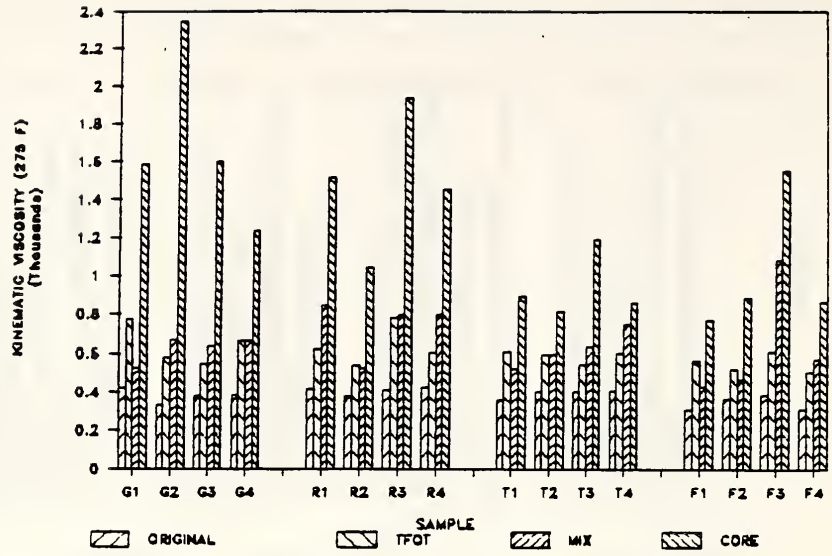

Figure 6-3. Changes in Kinematic Viscosity with Aging

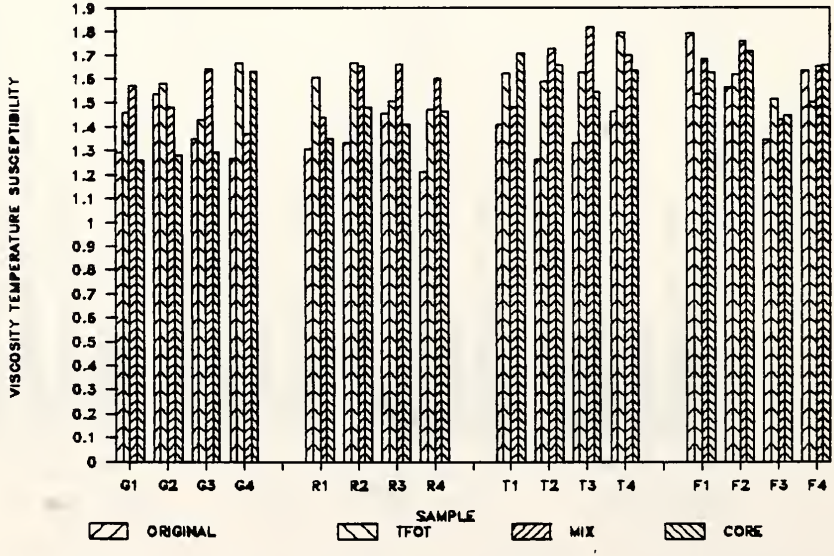

Figure 6-4. Changes in VTS with Aging

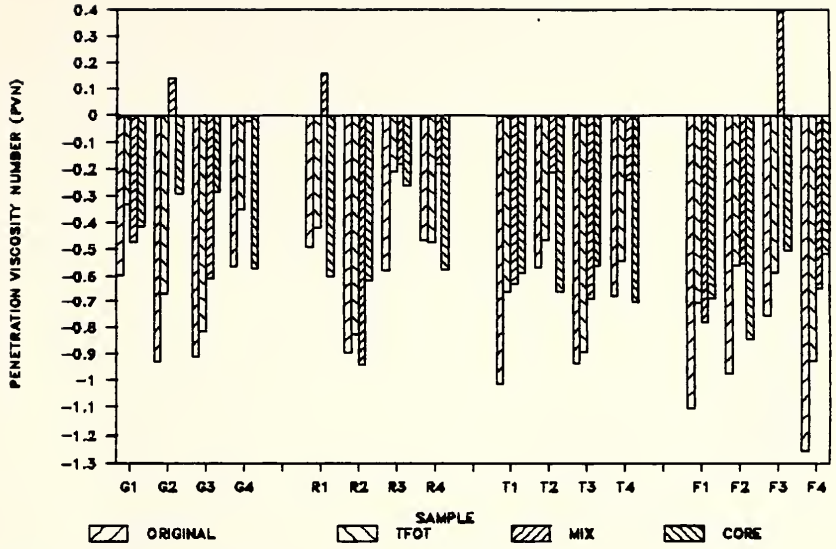

Figure 6-5. Changes in PVN with Aging

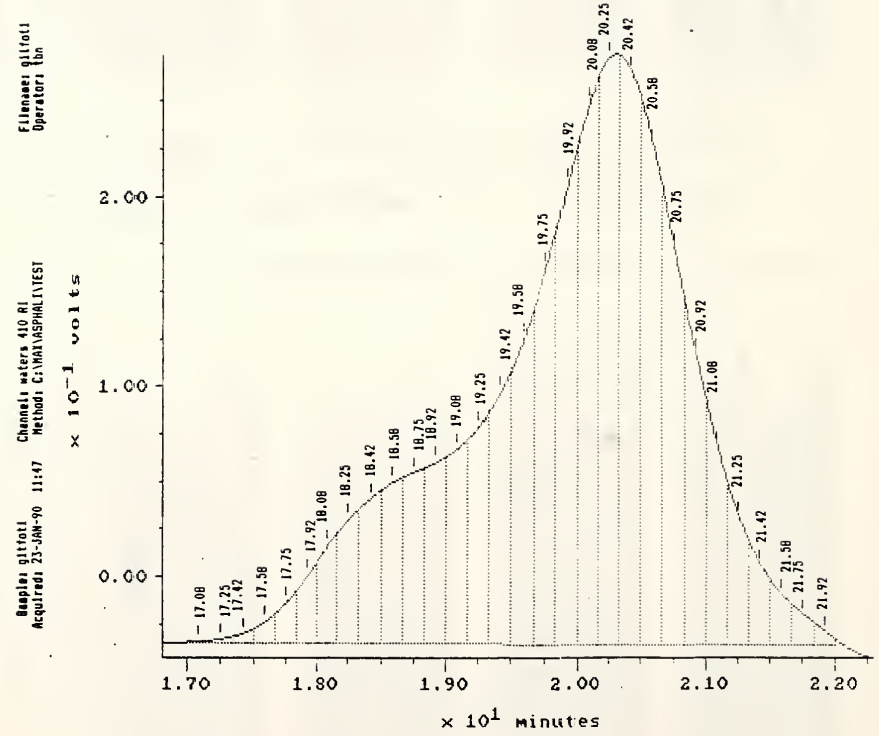

Figure 6-6. Chromatogram of Typical Asphalt After TFOT Aging

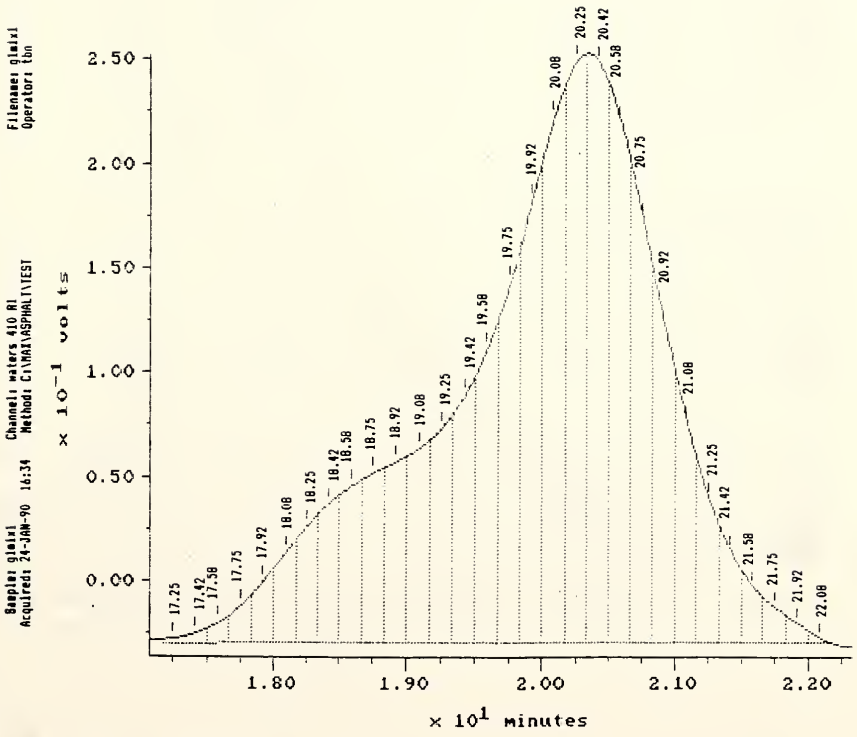

Figure 6-7. Chromatogram of Typical Asphalt After Aging in Asphalt Plant

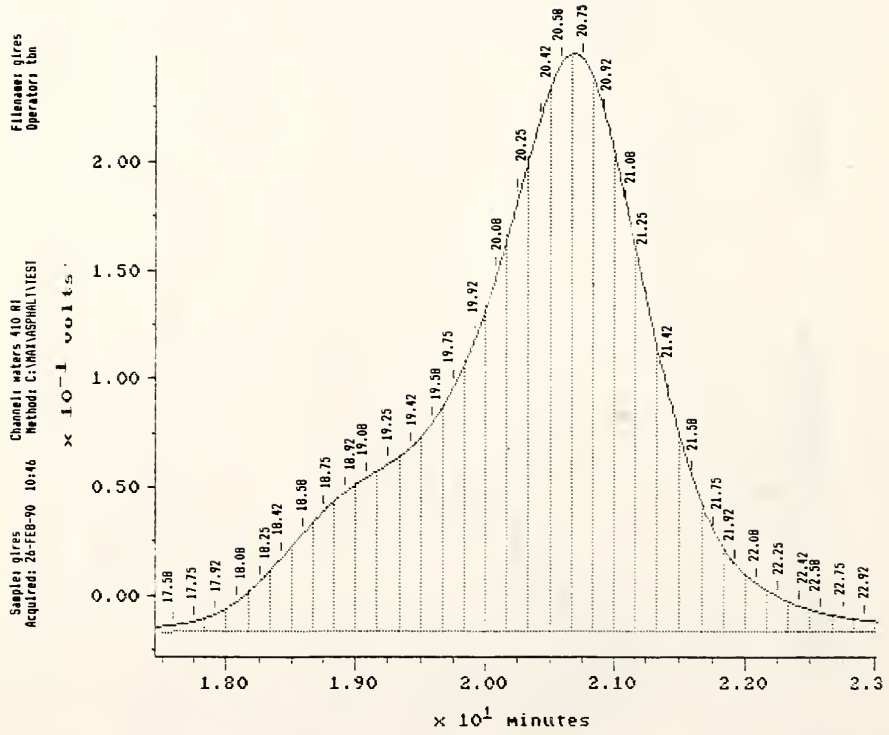

Figure 6-8. Chromatogram of Typical Asphalt After Aging Five Years in Pavement

Table 6-8. Chromatographic Parameters for TFOT Aged Samples

Sample	LMS	MMS	SMS	Mw	Mn	Polydis
G1	10.92	52.91	36.17	4146	604	6.866033
G2	12.70	50.01	37.29	4681	570	8.215481
G3	10.78	64.81	24.41	3564	655	5.443745
G4	14.20	59.55	26.25	4320	601	7.185721
R1	13.38	57.84	28.78	4080	545	7.484495
R2	11.14	59.00	29.86	4404	802	5.492429
R3	12.55	57.79	29.66	3896	560	6.956563
R4	11.38	55.44	33.18	3607	452	7.980669
T1	12.89	60.19	26.92	3979	614	6.480962
T2	10.57	58.90	30.53	3565	785	4.542437
T3	9.83	52.69	37.48	4128	586	7.04315
T4	10.42	63.44	26.14	3484	650	5.358442
F1	12.77	62.16	25.07	3350	646	5.185638
F2	10.25	52.92	36.83	3975	600	6.623147
F3	10.78	62.37	26.85	3511	642	5.470736
F4	10.23	52.25	37.52	3923	601	6.529504

Table 6-9. Chromatographic Parameters for Plant Aged Asphalt

Sample	LMS	MMS	SMS	Mw	Mn	Polydis
G1	12.97	57.81	29.22	3946	540	7.312396
G2	11.40	44.33	44.27	4234	477	8.885544
G3	7.36	40.60	52.04	3004	356	8.446861
G4	9.99	52.53	37.48	3087	397	7.779091
R1	11.81	51.40	36.79	4400	581	7.570096
R2	9.55	58.26	32.19	3981	726	5.485441
R3	12.74	64.94	22.32	3315	505	6.56564
R4	14.43	63.88	21.69	2903	364	7.977832
T1	10.08	64.57	25.35	3412	645	5.287727
T2	9.71	52.11	38.18	3829	577	6.636157
T3	10.60	63.21	26.19	3518	627	5.61186
T4	11.71	58.36	29.93	3650	517	7.062609
F1	11.10	59.73	29.17	3560	549	6.480647
F2	12.16	62.62	25.22	3205	668	4.796754
F3	9.83	52.69	37.48	3887	587	6.617734
F4	9.67	59.74	30.59	3235	554	5.83864

Table 6-10. Chromatographic Parameters for Samples Aged Five Years

Sample	LMS	MMS	SMS	Mw	Mn	Polydis
G1	14.07	69.36	16.57	2305	116	19.82929
G2	18.78	64.21	17.01	2476	20	121.0201
G3	14.43	65.96	19.61	1975	26	75.31674
G4	9.59	56.37	34.04	1995	182	10.97111
R1	15.14	73.44	11.42	1580	137	11.56535
R2	13.18	63.16	23.66	2718	371	7.315744
R3	12.69	71.38	15.93	2022	149	13.52544
R4	15.58	71.15	13.27	2555	179	14.25905
T1	10.07	53.63	36.30	2328	708	3.288804
T2	12.23	60.49	27.28	4985	256	19.450996
T3	10.26	57.13	32.61	3039	809	3.757260
T4	11.12	59.83	29.05	2294	239	9.597792
F1	9.16	55.60	35.24	2766	756	3.660046
F2	16.86	66.22	26.92	5206	294	17.731672
F3	7.60	57.87	34.53	2078	82	25.25427
F4	11.37	63.14	25.49	3584	503	7.129932

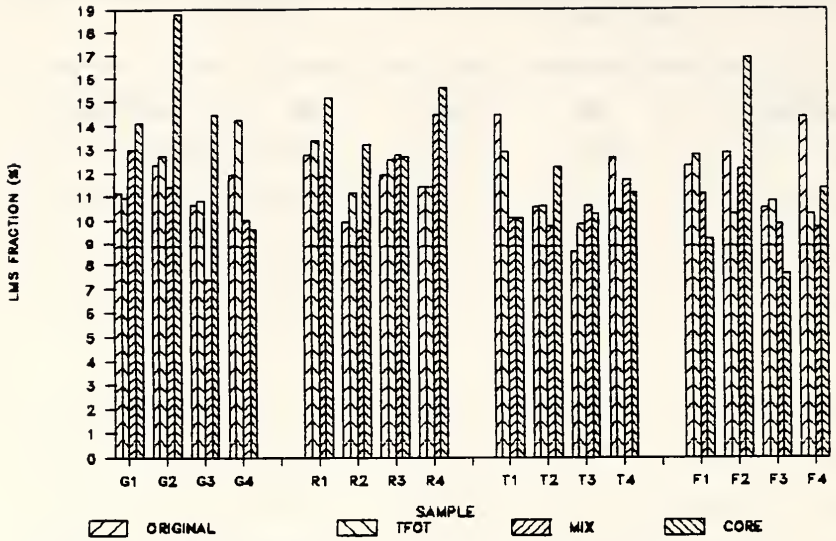

Figure 6-9. Comparison of LMS Fractions with Aging

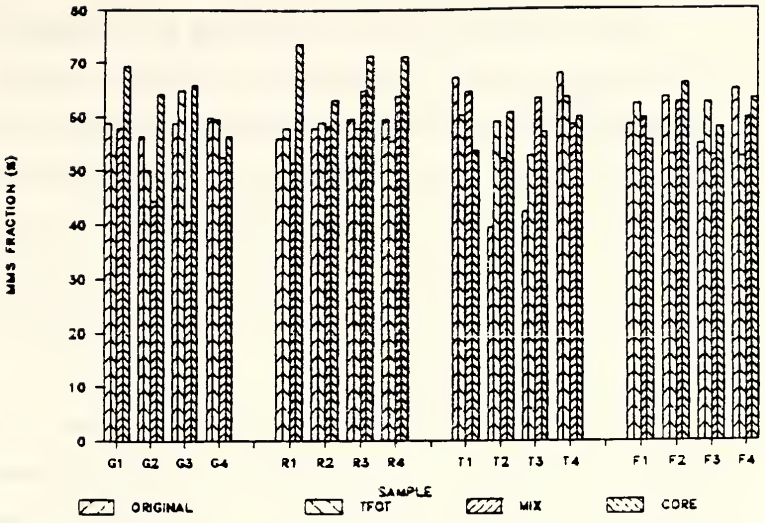

Figure 6-10. Comparison of MMS Fractions with Aging

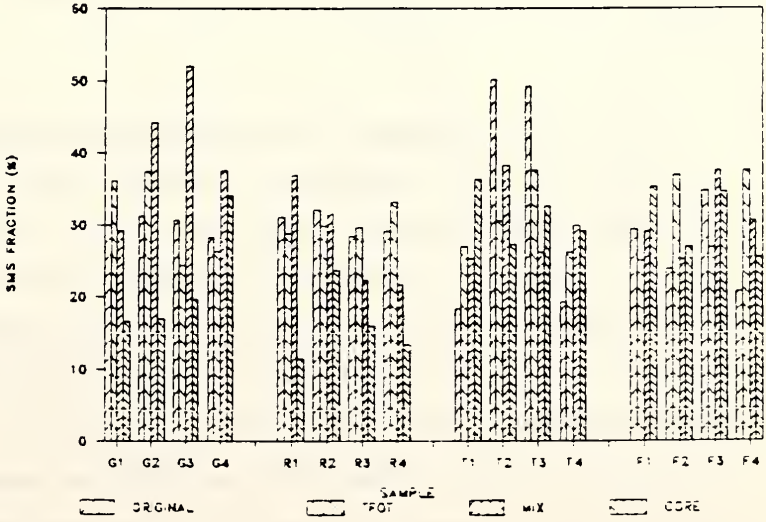

Figure 6-11. Comparison of SMS Fractions with Aging

A more visual analysis technique for comparing changes in chromatographic parameters through aging is the chromatogram overlay function available with the Maxima 820 software package. This function allows chromatograms for an asphalt at each of the four stages of aging to be compared to each other directly. Figure 6-12 shows an overlay of the four chromatograms taken at each stage of aging for the F3 asphalt.

The overlay in Figure 6-12 shows that the chromatogram changes with aging of the asphalt. With increased asphalt aging, the chromatogram's peak typically decreases in value, and the curve shifts to the right. This is a change typically found with all of the asphalts tested in this study.

6.3 - Aging of Asphalt in the Thin Film Oven Test

Review of the chromatogram overlays also indicated that the aging achieved in the thin film oven did not approximate the aging achieved in asphalt plants. This finding led to a preliminary study of the aging produced by the thin film oven test at varying times of exposure, as measured by both physical tests and HPGPC analysis.

This TFOT aging study was performed by exposing an original asphalt sample to the thin film oven aging for times varying from the ASTM standard of 5 hours up to 12.5 hours, increasing in 2.5 hour increments. At each

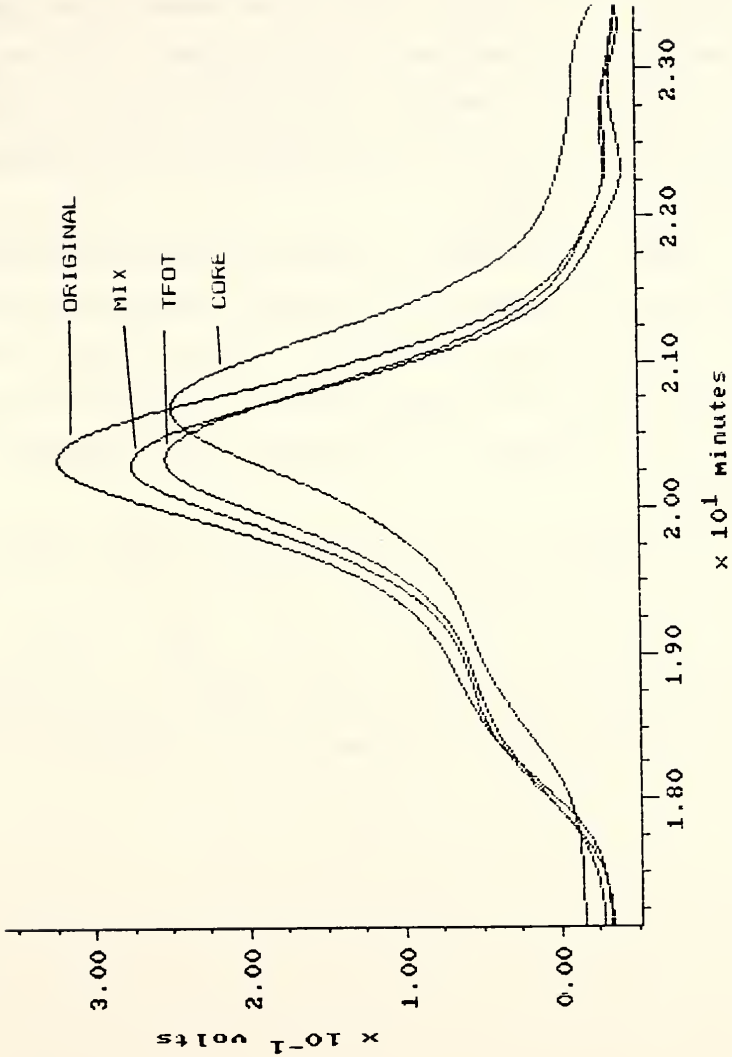

Figure 6-12. Overlay of Typical Asphalt Sample at Each Stage of Aging

increment of time, samples were removed from the oven and tested for penetration, absolute viscosity, and kinematic viscosity. Viscosity ratios and penetration retained values were also computed for the samples. The results of this testing are provided in Tables 6-11 and 6-12, with the corresponding values for the original, mix and core samples for the same asphalt.

Figure 6-13 shows the change in retained penetration for the five samples. The retained penetration decreases with increased TFOT exposure. Absolute and kinematic viscosities of the samples depicted in Figures 6-14 and 6-15, show increases in viscosity with increased TFOT exposure.

The samples were also analyzed by HPGPC techniques. The four TFOT samples (5 hr., 7.5 hr., 10 hr., 12.5 hr.) are overlaid in Figure 6-16. The commonly used chromatographic parameters of LMS, MMS, SMS, polydispersity and molecular weight averages are also presented in Table 6-13.

Table 6-11. Physical Parameters of Varying Aging in TFOT

Sample	Penetration	AVis (140°F)	KVis (275°F)
Original	50	2428.8	404.1
Mix	34	10496.1	633.4
Core	16	15149.0	1195.4
5 hr. TFOT	27	6578.6	533.5
7.5 hr. TFOT	20	10920.5	751.3
10 hr. TFOT	19	12142.8	828.1
12.5 hr. TFOT	15	14960.4	1168.7

Table 6-12. Age Hardening of Varying Exposure to TFOT

Sample	AVis Ratio	KVis Ratio	Pen Ret
Original	na	na	na
Mix	4.32	1.57	0.68
Core	6.24	2.96	0.32
5 hr. TFOT	2.71	1.32	0.54
7.5 hr. TFOT	4.50	1.86	0.40
10 hr. TFOT	5.00	2.05	0.38
12.5 hr. TFOT	6.16	2.89	0.30

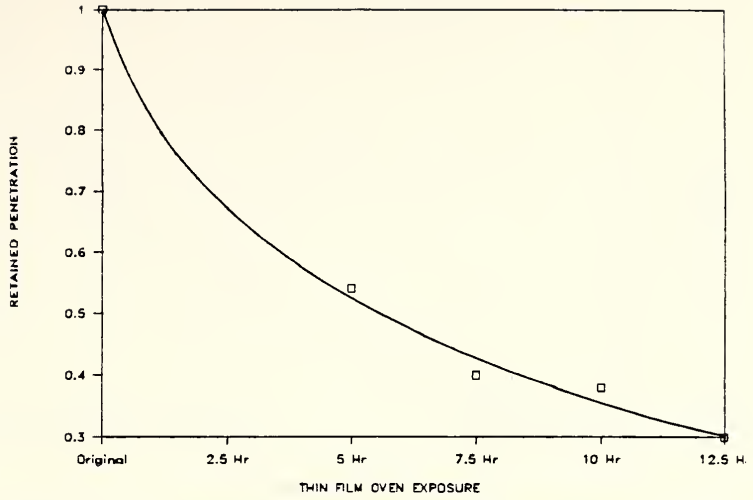

Figure 6-13. Changes in Penetration Retained for TFOT Samples

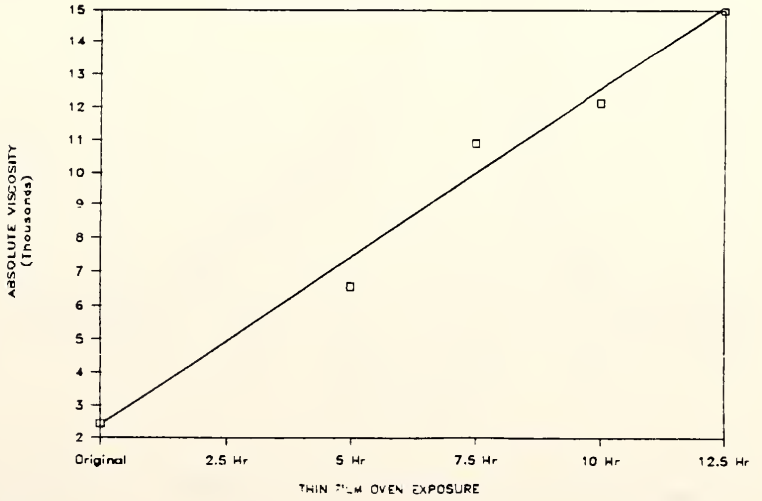

Figure 6-14. Changes in Absolute Viscosity for TFOT Samples

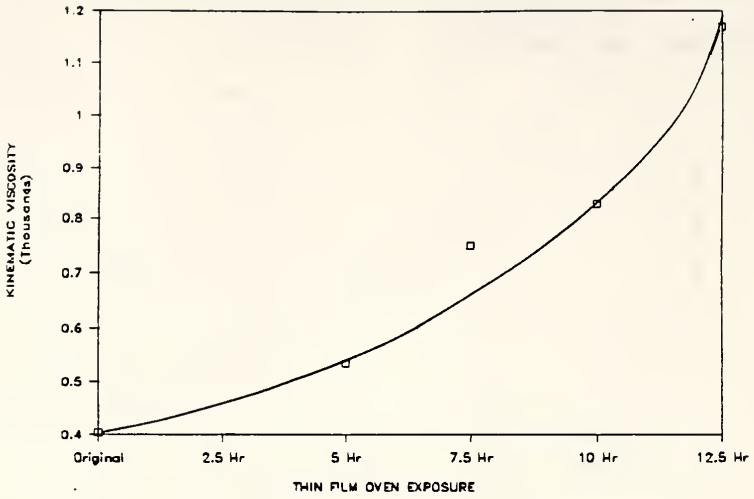

Figure 6-15. Changes in Kinematic Viscosity for TFOT Samples

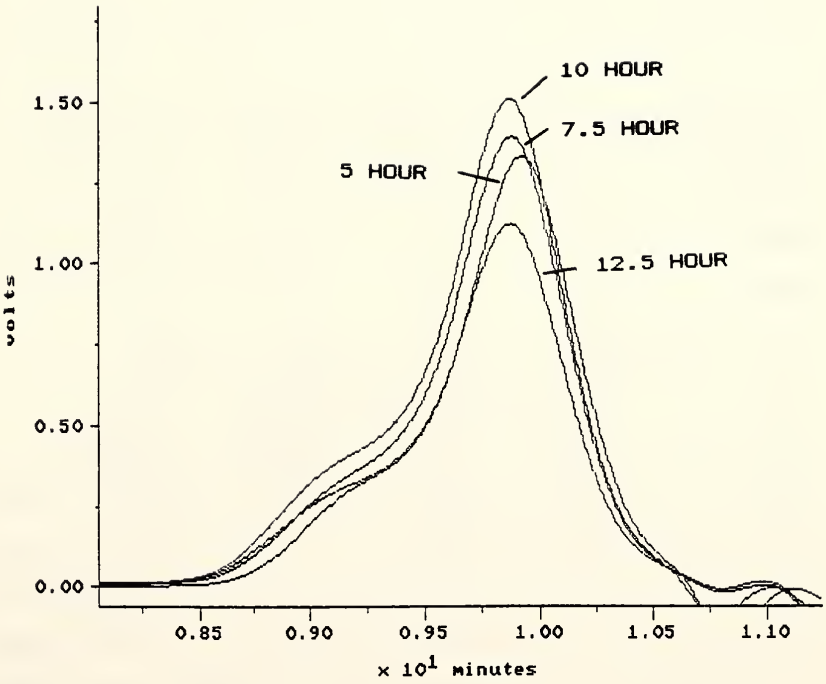

Figure 6-16. Overlay of TFOT Sample Chromatograms

Table 6-13. Chromatogram Parameters for TFOT Samples

Parameter	Original	Mix	Core
LMS	8.56	10.6	10.26
MMS	42.19	63.21	57.13
SMS	49.25	26.19	22.61
Mw	3016	3518	3039
Mn	578	627	809
Poly	5.2151	5.6119	3.7573
Mz	9405	12348	10880
Mz+1	18964	21360	20792

Parameter	5 Hour	7.5 Hour	10 Hour	12.5 Hour
LMS	7.4	9.46	11.25	11.63
MMS	50.93	55.71	55.56	55.06
SMS	41.67	34.83	33.19	33.31
Mw	2362	2827	3183	3258
Mn	660	785	821	799
Poly	3.5807	3.6037	3.8786	4.0796
Mz	8504	10067	11617	11949
Mz+1	16586	18929	21206	21640

CHAPTER 7

RESULTS: TESTS FOR FUEL CONTAMINATION

This chapter contains the results of tests performed to determine the effect of fuel contamination on the physical parameters of asphalt. The first section presents the results of tests on properties of uncontaminated and contaminated samples of each asphalt. The second section contains the results of chromatographic analysis of the uncontaminated and contaminated asphalts, and burner fuels. Finally, the third section compares the physical characteristics of mixes in both uncontaminated and contaminated conditions.

7.1 - Physical Tests of Uncontaminated and Contaminated Asphalts

Samples of asphalt extracted from the original mix that was processed in drum mix plants were contaminated with 1.0% burner fuel. Each asphalt was contaminated with the burner fuel that was collected from that particular asphalt plant. The physical parameters of the contaminated asphalt were measured, and compared to the properties of the uncontaminated samples. These parameters are listed in Tables 7-1 and 7-2, and are discussed in the paragraphs that follow.

Table 7-1. Physical Parameters of Uncontaminated Asphalt

Sample	Pen	KVis	AVis	PVN	VTS
R2	34	521.9	5870.7	-0.94	1.65
R3	42	801.6	10857.8	-0.18	1.66
T2	60	597.7	8189.3	-0.21	1.73
T4	43	752.4	10846.0	-0.24	1.70
F2	60	469.4	6179.1	-0.55	1.76
F4	41	574.9	6665.3	-0.65	1.65

Table 7-2. Physical Parameters of Contaminated Asphalt

Sample	Pen	KVis	AVis	PVN	VTS
R2	33	590.2	5524.9	-0.81	1.52
R3	43	876.8	10124.7	-0.04	1.55
T2	62	580.4	9200.8	-0.22	1.82
T4	40	727.7	10547.3	-0.36	1.72
F2	56	614.2	7129.9	-0.25	1.63
F4	48	588.1	8004.8	-0.46	1.73

7.1.1 - Penetration

Penetration values for all samples in both the uncontaminated and contaminated conditions are shown in Figure 7-1. Penetration values for the asphalt samples did not change in any consistent manner. Penetration values for three asphalts, one of each burner fuel type, increased, and the other three decreased. Penetrations did not change by more than 17% between the contaminated and uncontaminated state for any sample.

7.1.2 - Viscosity

Values for Kinematic and Absolute Viscosity both showed an inconsistency similar to that of penetration, as shown in Figures 7-2 and 7-3. As with penetration, half of the values for absolute viscosity increased, while the others decreased. For Kinematic Viscosity, four increased while two decreased. No consistent relationship of increase or decrease of viscosities could be found for a given asphalt at the two test temperatures. The amount of viscosity change for any given asphalt is small, however, with nine of the twelve changes being less than a 10% difference, and only one difference over 25%.

7.1.3 - Temperature Susceptibility

The temperature susceptibility indices of viscosity-temperature susceptibility (VTS) and penetration viscosity number are depicted in Figures 7-4 and 7-5, respectively. VTS values show differences between uncontaminated samples

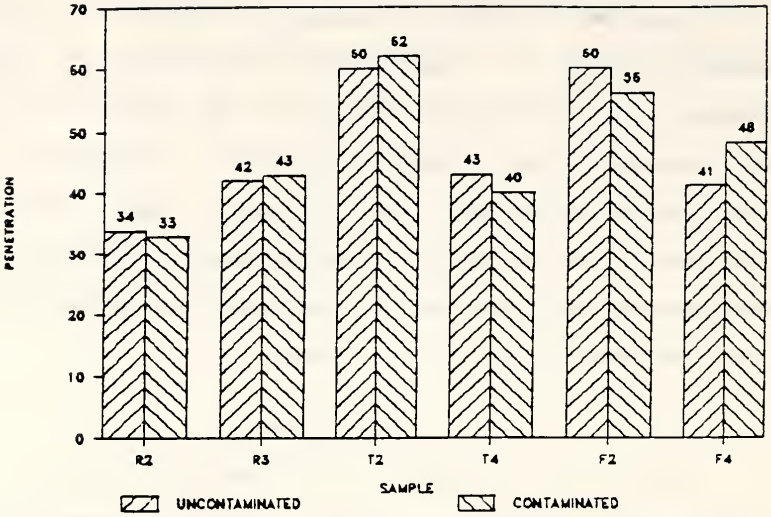

Figure 7-1. Penetration of Fuel Contamination Samples

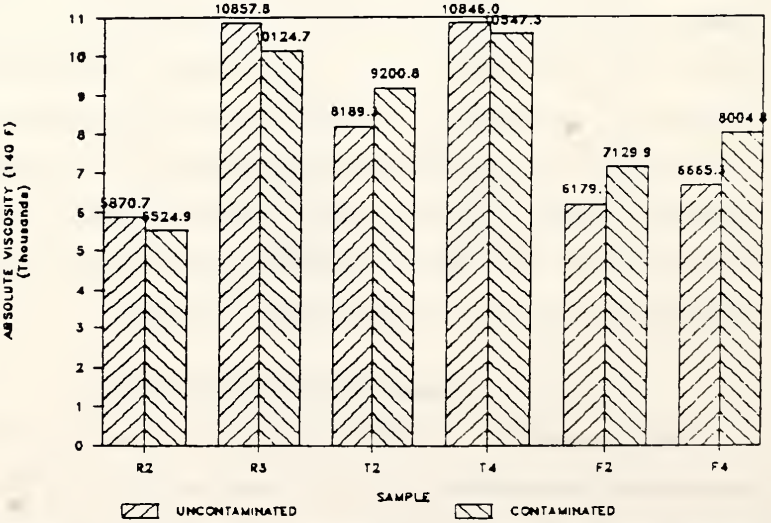

Figure 7-2. Absolute Viscosity of Fuel Contamination Samples

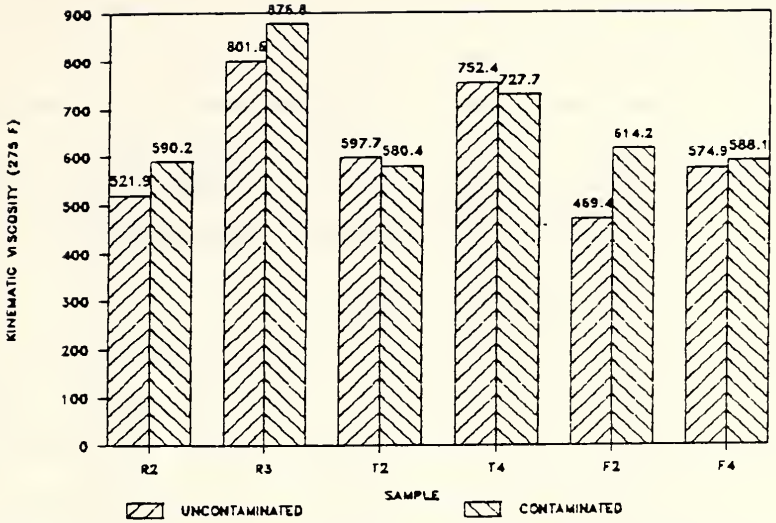

Figure 7-3. Kinematic Viscosity of Fuel Contamination Samples

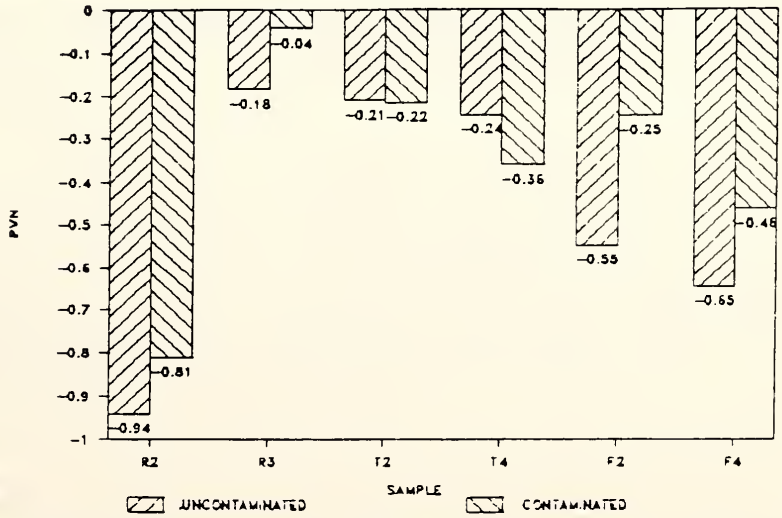

Figure 7-4. Penetration Viscosity Number for Fuel Contamination Samples

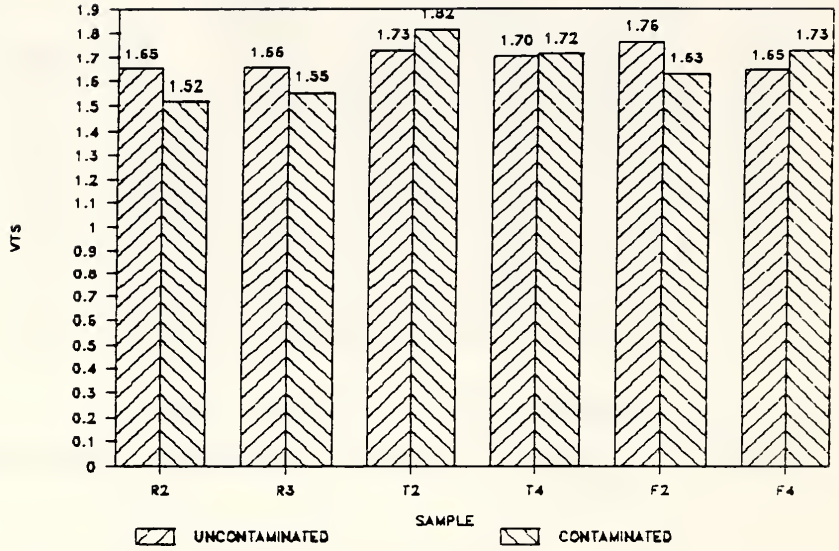

Figure 7-5. Viscosity-Temperature Susceptibility of Fuel Contamination Samples

and contaminated samples of less than 9% for all samples, with increases and decreases divided evenly among samples. PVN values, although showing larger differences, show no consistency in increases or decreases in values.

7.2 - Chromatographic Analysis of Uncontaminated and Contaminated Samples and Their Burner Fuels

7.2.1 - Asphalt Samples

The previously tested samples of contaminated asphalt were analyzed by HP-GPC techniques and compared to the chromatograms already obtained for uncontaminated samples of the same asphalt. Figure 7-6 shows an overlay of a typical asphalt sample (T2) in both the uncontaminated and contaminated conditions. The contaminated asphalt sample shows a shift in the chromatogram to the right with a more gradual tailing of the SMS molecules. The other asphalt samples studied, included in Appendix C, show this same tendency for all samples.

Slices of the areas under the curve were taken for the chromatograms, and the results of the area calculations and curve parameters for the uncontaminated and contaminated asphalts are shown in Tables 7-3 and 7-4. These results are discussed in the paragraphs that follow.

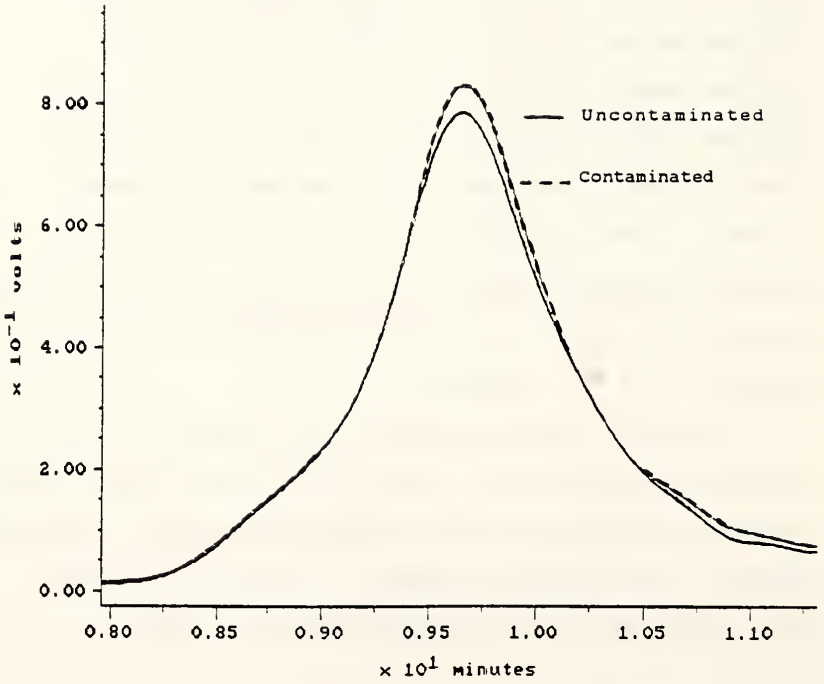

Figure 7-6. HPGPC Overlay of Uncontaminated and Contaminated Asphalt (T2)

Table 7-3. HPGPC Values for Uncontaminated Asphalt

	R2	R3	T2	T4	F2	F4
LMS%	9.55	12.74	9.71	11.71	12.16	9.67
MMS%	58.26	64.94	52.11	58.36	62.62	59.74
SMS%	32.19	22.32	38.18	29.93	25.22	30.59
Mw	3981	3315	3829	3650	3205	3235
Mn	726	505	577	517	668	554
Poly.	5.4854	6.5656	6.6362	7.0626	4.7968	5.8386
Mz	13684	12191	14419	13500	9963	12005

Table 7-4. HPGPC Values for Contaminated Asphalt

	R2	R3	T2	T4	F2	F4
LMS%	11.24	17.18	14.76	22.57	17.11	15.24
MMS%	61.93	70.59	68.07	64.95	68.73	65.85
SMS%	26.83	12.23	17.17	22.48	14.16	18.91
Mw	5305	4313	4703	6024	4149	5973
Mn	562	41	157	428	235	355
Poly.	9.4485	105.9384	29.8612	14.0710	17.6171	16.8357
Mz	23150	20860	23671	27637	16831	27403
Mz+1	44538	39702	44101	51325	32197	50483

The changes in size fractions between uncontaminated and contaminated samples of the asphalts are shown in Figures 7-7, 7-8 and 7-9, for LMS, MMS, and SMS fractions respectively. These figures show a consistent relationship between the fractions of the uncontaminated asphalt samples and the fractions of the contaminated samples. The molecular size fractions of LMS and MMS increase when the sample is contaminated, and the SMS fraction decreases in percent when the asphalt is contaminated. The amount of change in fractional percents is most notable with the SMS fraction, ranging in value from a 16.6% to 55.0% decrease.

The chromatograph curve parameters also show a consistent change between uncontaminated and contaminated samples. The number average molecular weight (Mn), shown in Figure 7-10 decreases for each sample, and the weight average molecular weight (Mw), shown in Figure 7-11, increases for each sample. The amount of each decrease/increase is significant in quantity, ranging in value from 17.2 to 91.7 percent.

The parameters of z-average molecular weight (Mz), z+1-average molecular weight (Mz+1) and polydispersity also show measurably different increases between uncontaminated samples and contaminated samples for each of the asphalts studied. These parameters are shown in Figures 7-12, 7-13, and 7-14, respectively.

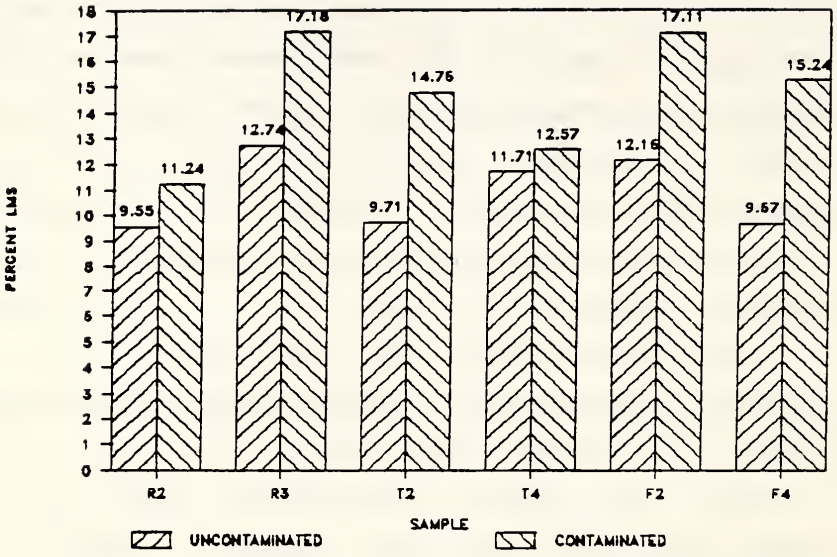

Figure 7-7. Percent LMS Fraction for Fuel Contamination Samples

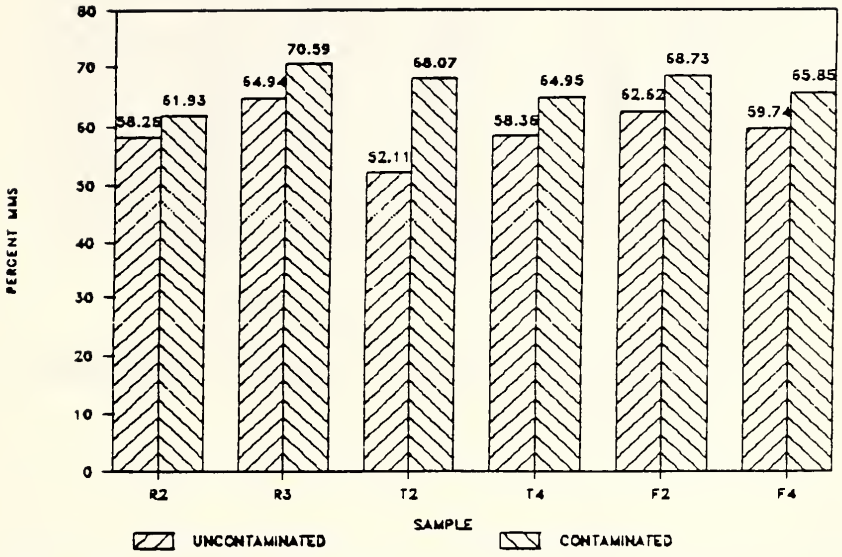

Figure 7-8. Percent MMS Fraction for Fuel Contamination Samples

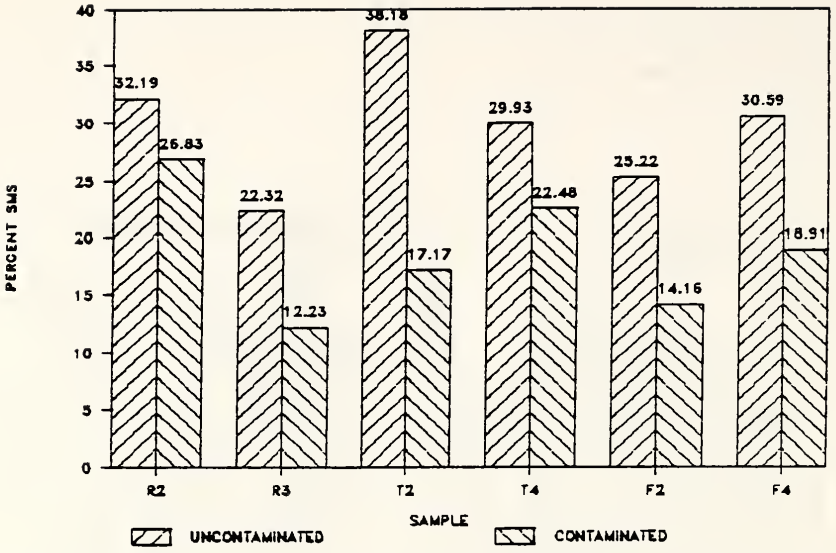

Figure 7-9. Percent SMS Fraction for Fuel Contamination Samples

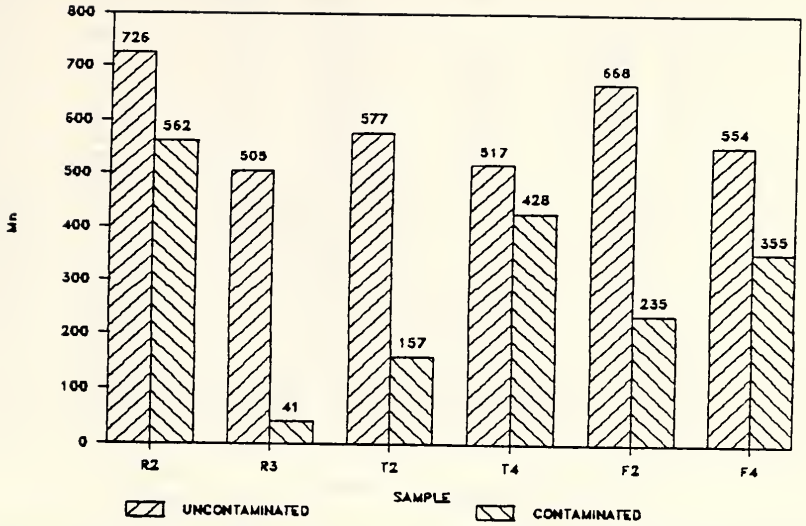

Figure 7-10. Number Average Molecular Weight (Mn) for Fuel Contamination Samples

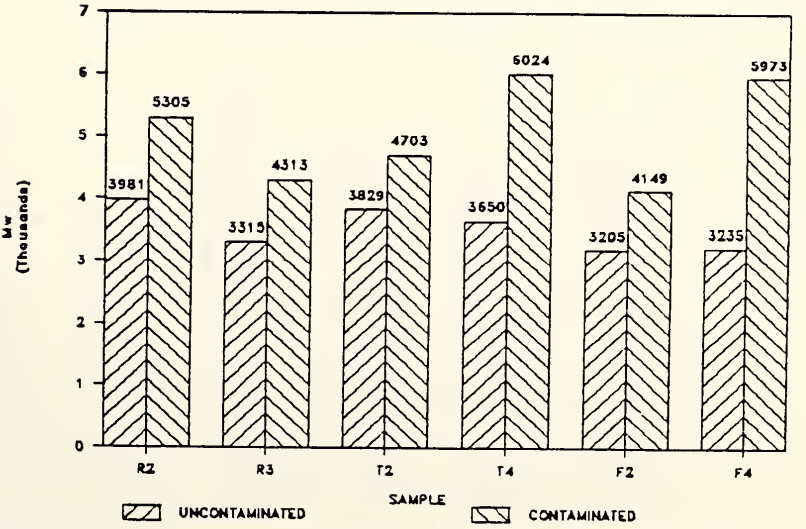

Figure 7-11. Weight Average Molecular Weight (Mw) for Fuel Contamination Samples

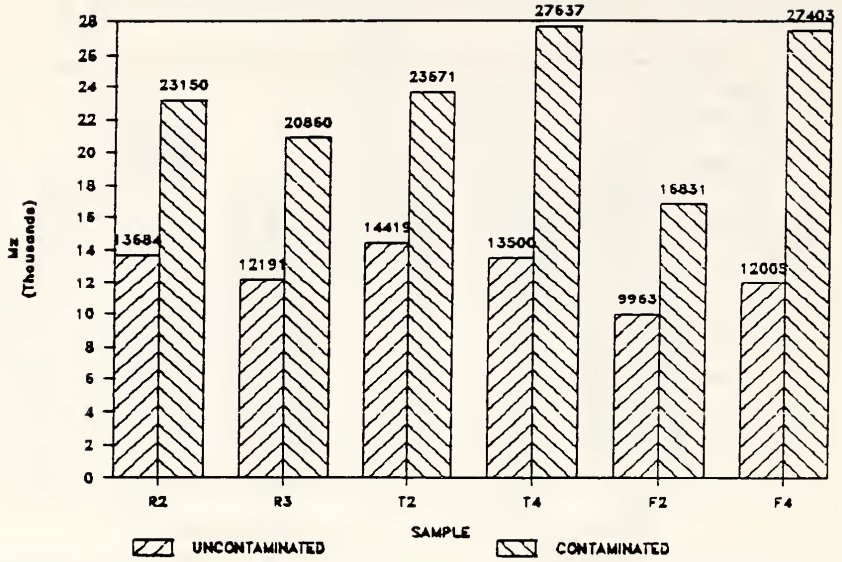

Figure 7-12. Mz Values for Fuel Contamination Samples

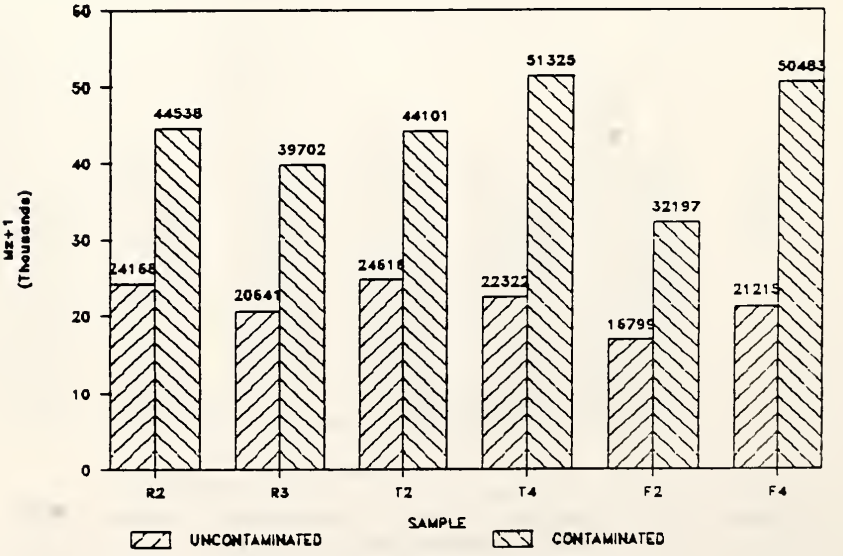

Figure 7-13. Mz+1 Values for Fuel Contamination Samples

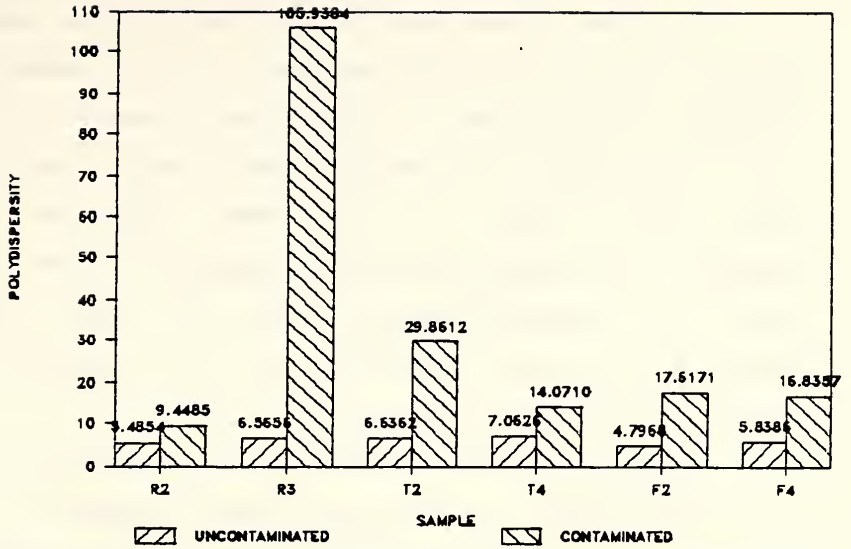

Figure 7-14. Polydispersity Values for Fuel Contamination Samples

7.2.2 - Burner Fuels

The burner fuels used to contaminate the asphalt samples in this study were analyzed by HP-GPC techniques. A typical chromatogram of a burner fuel is shown in Figure 7-15. The breadth of the chromatogram is small, indicating that burner fuels are narrow band, molecular sized materials. The peak of these chromatograms is close to the peak of the asphalt samples, which, due to the additive nature of molecular size fractions, would increase the values of LMS and MMS fractions.

Figure 7-16 shows a chromatogram generated by adding the chromatogram of an uncontaminated asphalt to the chromatogram of the burner fuel used to produce that asphalt mix. The resulting chromatogram shows properties similar to that of a contaminated asphalt, indicating the additive property of chromatograms.

7.3 - Tests of Mixes

Uncontaminated original mixes and contaminated mixes produced by adding 1% burner fuel to the original mix were also tested in order to determine whether the effects of fuel contamination in the resulting mixes could be detected. Table 7-5 shows the results of tests of Marshall Stability and Flow, and of Indirect Tension testing.

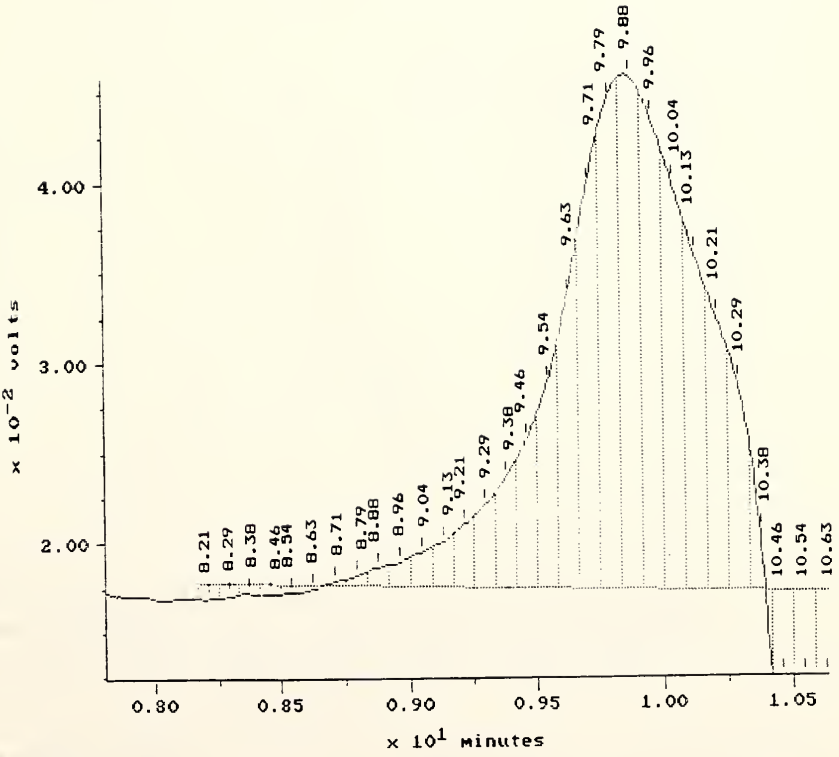

Figure 7-15. Chromatogram of Typical Burner Fuel

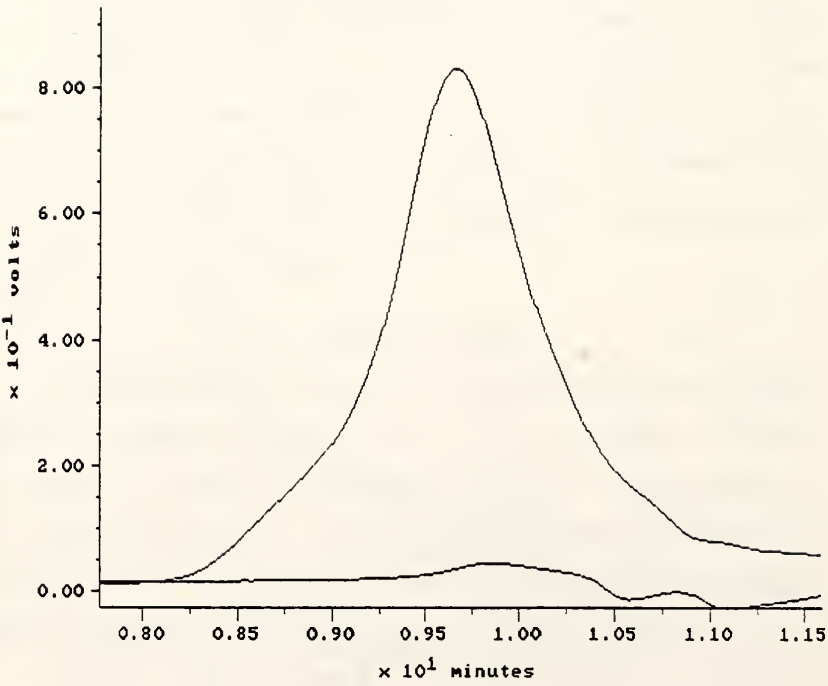

Figure 7-16. Chromatogram of Asphalt and Burner Fuel Combination

Table 7-5. Test Results of Uncontaminated and Contaminated Mixes

Sample	Ind Tens	Stab	Flow
		Uncontaminated Mixes	
R2	172.2	3810	11
R3	159.1	3460	8
T2	212.1	4511	12
T4	215.1	4008	11
F2	200.5	1138	7
F4	230.2	1280	8
		Contaminated Mixes	
R2	164.6	3800	12
R3	169.0	3210	12
T2	201.3	4076	13
T4	214.7	3814	8
F2	245.5	1695	8
F4	219.4	1296	7

Tests of Marshall Stability and Flow, shown in Figures 7-17 and 7-18, respectively, show no consistent relationship with fuel contamination. Two of the samples increase in stability with contamination, while four decrease in value. Flow values increase for four of the samples, while two decrease in flow.

When samples were reheated, recompacted, and measured for indirect tensile strength, two of the samples shows increased tensile strength, while four samples show decreased strength. These values are shown in Figure 7-19.

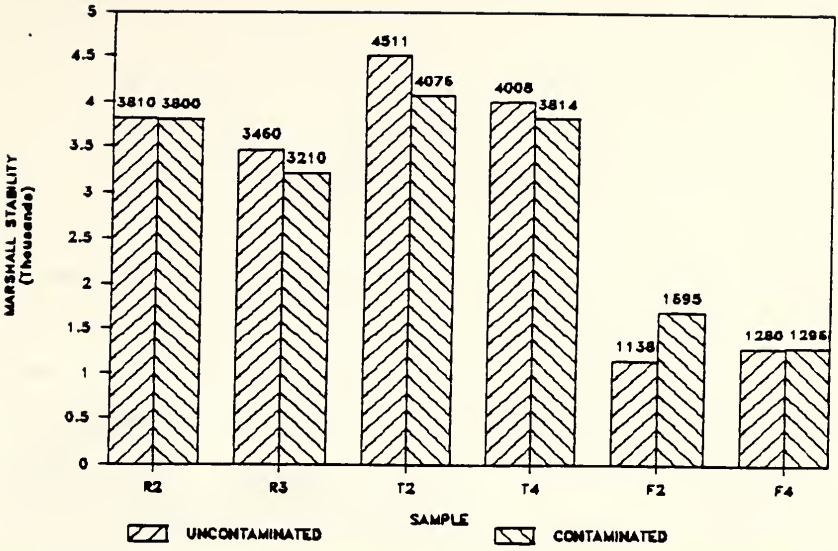

Figure 7-17. Marshall Stability of Fuel Contamination Samples

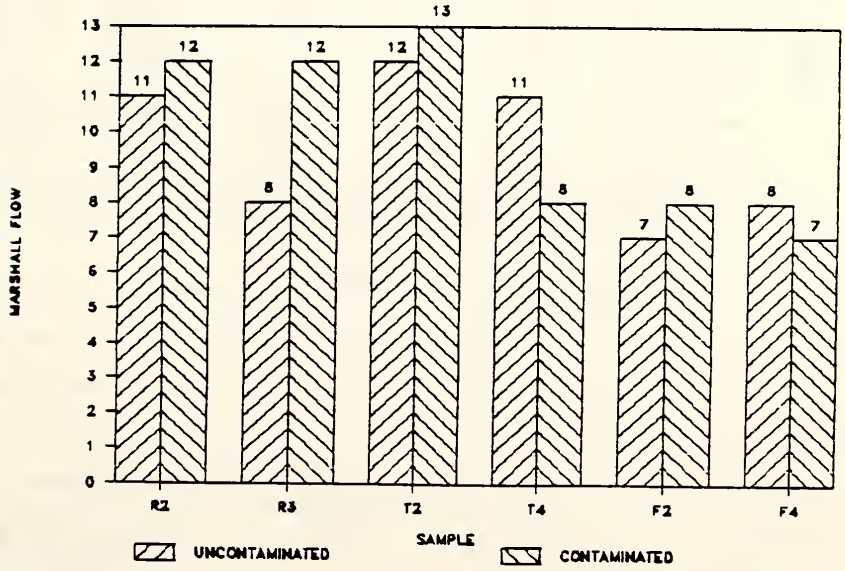

Figure 7-18. Marshall Flow of Fuel Contamination Samples

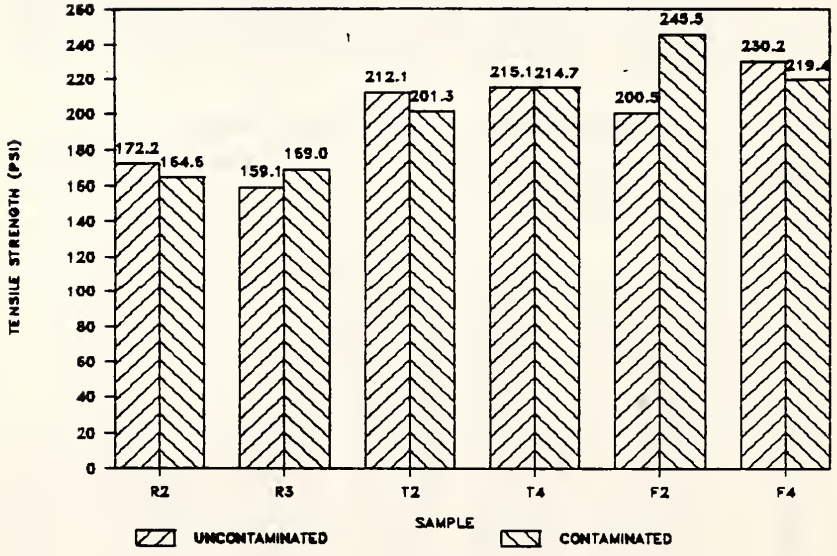

Figure 7-19. Indirect Tensile Strength of Fuel Contamination Samples

CHAPTER 8

DISCUSSION OF RESULTS

This chapter presents a discussion of the results of the tests reported in the previous three chapters. The first section discusses the relationships between physical parameters of asphalts and characteristics of their chromatograms. The second section discusses the evaluation of effects of aging on the physical parameters of asphalts and the chromatograms. This section also includes the effects of different plant types and burner fuels on asphalt mixes. The final section discusses the effects of fuel contamination upon physical parameters and chromatograms of asphalt.

8.1 - Discussion of Tests of Asphalt Parameters

Data from tests on the original asphalt are presented in Chapter 5. This data was used to compare physical parameters of asphalts with chromatographic parameters to determine whether apparent correlations exist.

The first method of comparison involved plotting each of the nine physical parameters with each of the ten chromatographic parameters. This resulted in 90 plots, which are filed with the database of chromatograms. A sample plot is shown in Figure 8-1. This plot depicts

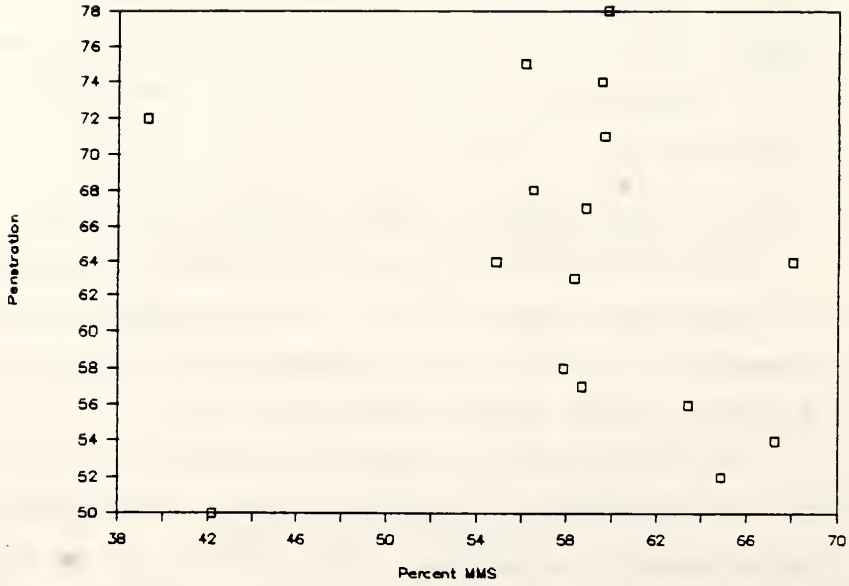

Figure 8-1. Plot of Penetration vs. MMS Fraction

penetration plotted against MMS fraction. No relationship between the two parameters is apparent in this plot. Figure 8-2 presents a plot of absolute viscosity (AVis) versus weight-average molecular weight (Mw). This plot also shows no readily apparent correlation between the two measures. None of the plots shows any readily evident correlation between parameters.

Although plots of the physical measures versus chromatographic measures show no apparent correlation between the parameters, a more analytical evaluation of correlations is the Pearson Correlation Coefficient (r), as described in Chapter 4. Pearson coefficients for each of the comparisons are given in Table 8-1. Values of r close to 1 or -1 indicate strong correlations, while values of r close to 0 indicate little or no correlation.

A level of significance of .95 (which means that there is a 5% chance of a correlation showing when such a correlation may not exist) and 14 degrees of freedom (no. of samples -2) established the critical value of r for significant correlations as $\pm$ 0.4973 [67]. Any absolute values of r greater than this critical value indicates that a correlation exists between the two parameters. At the .95 level of significance, correlations exist for the eight relationships shown in Table 8-2. At the .98 level of significance (r=.5742), six correlations are significant, and at the .99 level (r=.6226), only three correlations are significant. These correlations for the levels of

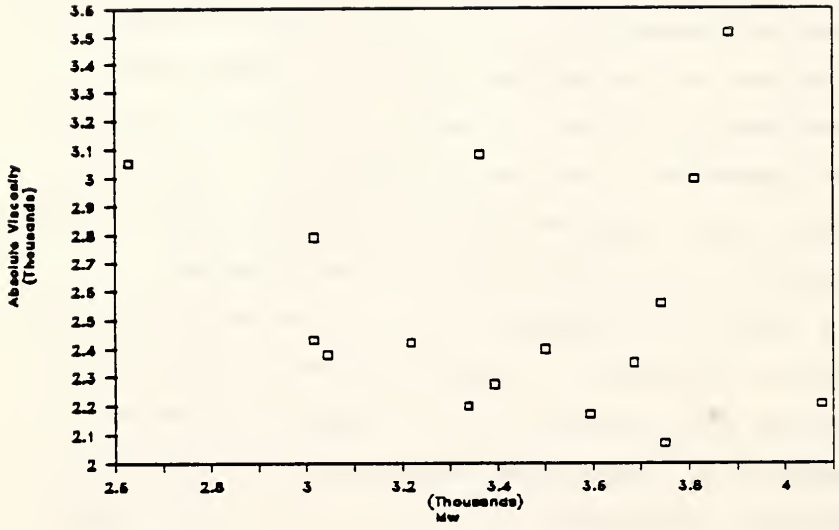

Figure 8-2. Plot of Absolute Viscosity vs. Mw

Table 8-1. Pearson Correlation Coefficients for Original Asphalt

	Sp Grav	Pen	KVisc	AVisc	PVN	VTS	Pen Ret	KVis Rat	AVis Rat
LMS	-0.09195	-0.00714	-0.44764	0.398591	-0.27296	0.50541	0.118802	-0.13231	0.374749
MMS	-0.02815	-0.12195	-0.27387	0.35152	-0.22623	0.370585	-0.01525	-0.05594	0.293074
SMS	0.040394	0.106798	0.315067	-0.37372	0.242285	-0.40884	-0.0075	0.071482	-0.31898
Mw	-0.13755	0.195458	0.470257	-0.69293	0.407885	-0.66947	-0.2195	0.436596	-0.21735
Mn	-0.16436	-0.35489	-0.17249	-0.01134	-0.30463	0.080578	-0.03648	-0.23396	-0.08543
Poly	0.384214	0.598	-0.01497	-0.04374	0.332871	-0.03496	-0.58199	0.188766	0.40978
Mz	0.421733	0.448053	-0.0964	-0.04341	0.195828	-0.00268	-0.66212	0.051549	0.435329
Mz+1	0.454915	0.344582	-0.08449	-0.03937	0.144165	-0.00744	-0.5911	0.031213	0.373155
MzRat	0.404591	0.511952	0.077151	0.043892	0.332607	-0.0407	-0.47482	0.125819	0.360989
Mz+1Rat	0.439441	0.242706	0.097967	0.050959	0.190464	-0.04623	-0.30196	0.066179	0.208154

Table 8-2. Significant Correlations

Physical Para.	Chromatogram Para.	Pearson Coef.
Penetration Retained	Polydispersity	-0.58199*
Penetration Retained	Mz	-0.6212**
Penetration Retained	Mz+1	-0.59110*
Penetration	Polydispersity	0.598000*
Penetration	Mz/Mw	0.511952
Absolute Viscosity	Mw	-0.69293**
VTS	LMS	0.50541
VTS	Mw	-0.66947**

* significant at .98 level

** significant at .99 level

significance are indicated in Table 8-2 with asterisks.

Evaluation of the significant correlations shows that none of these is apparent by the plots. For example, Figure 8-2, which depicts absolute viscosity plotted versus molecular weight (Mw), shows no apparent relationship, but generates the strongest correlation significant at the .99 level.

One point of interest is that only one of the commonly used chromatographic measures, the large molecular size fraction (LMS) shows any correlation with a physical parameter, viscosity-temperature susceptibility (VTS). All other significant relationships involve molecular weights or the polydispersity of the chromatogram. Correlations between chromatograms and the measures of penetration and penetration retained have not been reported previously by researchers. Absolute viscosity also has not been shown by past research to relate to chromatograms. Temperature susceptibility is the only measure to have been found by Garrick [15,57] and Price [16] to show correlations with chromatograms. None of these correlations can be interpreted as being strong, however, as evidenced by the magnitude of the Pearson coefficients.

A second point which may be significant is that the Pearson correlation coefficients for LMS and MMS have the same sign, while SMS has the opposite sign when compared to each physical parameter except penetration retained. This would indicate that physical parameters vary in the same

manner for LMS and MMS changes, while varying in the opposite manner for SMS changes. This relationship should be examined in more detail for significance.

During the conduct of this phase of the study, one issue did arise which may be of further interest for researchers involved with chromatographic analysis. At one point in running injections, an equipment malfunction caused a delay of two hours in making an injection of a prepared sample. The resulting chromatogram, contrary to findings presented by other researchers [16,62], did not indicate any adverse disassociation of agglomerated molecules as would be evidenced by changes in size fractions. This finding was further evaluated by preparing a sample according to the procedures developed by Jennings [61] and modified for this specific equipment. Analysis was performed at several time intervals.

In these tests, the first injection of the sample was made immediately after preparation. Ensuing injections were made at 1 hour, 2 hours, 4 hours, 8 hours, 12 hours and 24 hours after preparation. An overlay of the chromatograms, shown in Figure 8-3, indicates little difference among the runs. The chromatographic data is presented in Table 8-3. The results show that the sample has changed negligibly. This is plotted in Figures 8-4 and 8-5, which show size fractions and molecular weights of the samples, respectively. This consistency would indicate that, for this asphalt, no disassociation of molecules

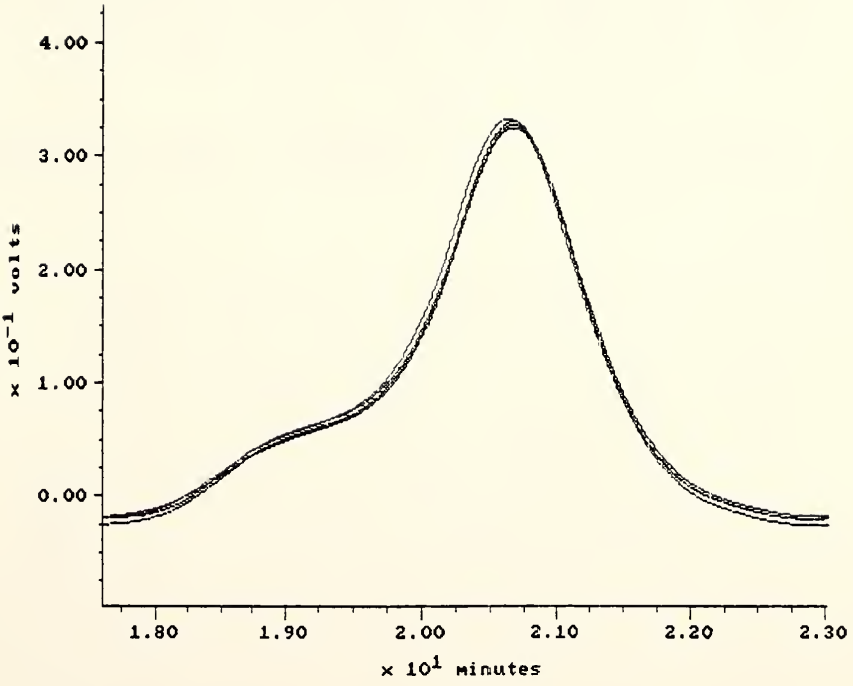

Figure 8-3. Overlay of Chromatograms of One Asphalt Sample at Various Ages

Table 8-3. Chromatographic Data for Samples Injected at Various Time Intervals

Sample Age	LMS	MMS	SMS	Mw	Mn	Poly
Original	9.25	50.54	40.21	3694	543	6.8046
1 Hr.	9.89	50.57	39.54	3833	561	6.8354
2 Hrs.	9.28	51.62	39.10	3676	572	6.4304
4 Hrs.	10.01	51.72	38.27	3921	585	6.7020
8 Hrs.	9.68	51.26	39.06	3781	585	6.4670
12 Hrs.	10.08	50.74	39.18	3909	584	6.6890
24 Hrs.	10.51	50.16	39.33	3998	588	6.8003

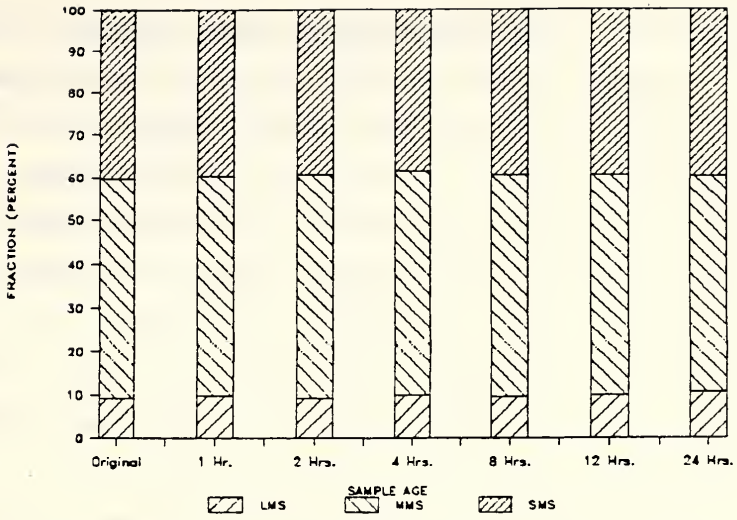

Figure 8-4. Sample Composition of Samples Injected at Various Intervals

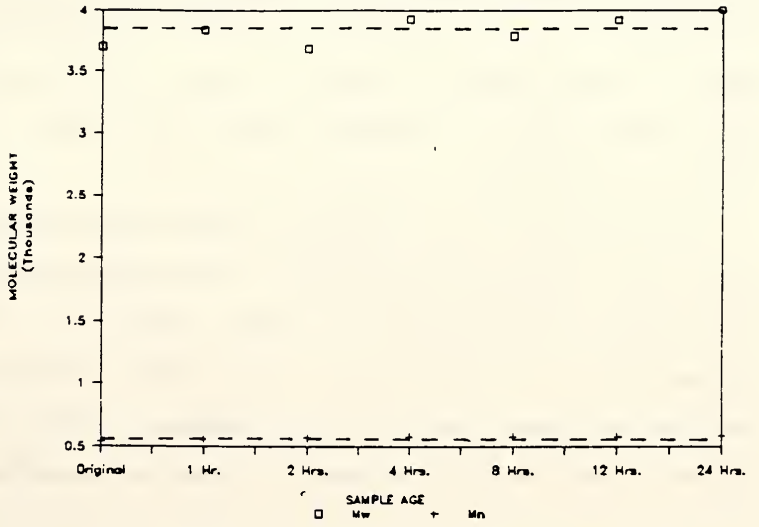

Figure 8-5. Molecular Weights of Samples Injected at Various Intervals

occurs within 24 hours of preparation of the solution.

8.2 - Discussion of Tests on Aging

Changes in the physical parameters of the asphalt due to aging were analyzed through analysis of variance procedures (ANOVA). All of the physical measure changes that were analyzed detected significant changes in the asphalt in the four different stages. A summary of the results of the statistical evaluation of physical parameters is presented in Table 8-4. The F values are large for all physical measures that were evaluated, resulting in low p-values and high significance.

Evaluation of chromatographic measures for detecting changes in asphalt with aging was not as successful as physical measures. One of the chromatographic measures evaluated did not detect significant changes due to aging differences. Of significance is the fact that LMS did not detect changes between stages of aging. This measure is the chromatographic measure most often cited in the evaluation of aging.

The results of the ANOVA of chromatographic properties are shown in Table 8-5. At the .05 significance level, LMS accepts the hypothesis of equal means, not detecting differences in LMS with aging. The other chromatographic measures all show significant differences, although the F-values are not as high as those for physical measures.

Table 8-4. ANOVA Results for Physical Changes With Aging

Physical Measure	F-value	p-value	Significant?
Penetration	124.12	.0001	Yes
Kin. Viscosity (275°F)	4.18	.0132	Yes
Abs. Viscosity (140°F)	57.85	.0001	Yes
Visc. Ratio (275°F)	24.84	.0001	Yes
Visc. Ratio (140°F)	91.30	.0001	Yes
PVN	7.64	.0005	Yes
VTS	7.57	.0006	Yes
Penetration Retained	226.50	.0001	Yes

Table 8-5. ANOVA Results for Chromatographic Changes with Aging

Chromatographic Measure	F-value	p-value	Significant?
LMS	2.43	.0831	No
MMS	3.48	.0272	Yes
SMS	3.78	.0199	Yes
Mn	23.19	.0001	Yes
Mw	4.35	.0112	Yes
Poly	13.96	.0001	Yes

An additional objective of the study was to evaluate whether differences could be detected between types of asphalt plants or fuels used to heat and dry the aggregate. No consistency in detecting any of these differences could be found. The major effect of plant type was only evaluated as significant at the .10 level for one measure (Mw). The major effect of fuel used in the drier was reported as significant at the .10 level by only two of the measures (POLY, LMS). A summary of significant major effects and interactions is presented in Table 8-6.

These results indicate that the effects/interactions of fuel and plant type do not significantly alter the asphalt parameters, or that the level of fuel in the asphalt is below the level that can be detected by either physical or chromatographic measures. The fact that the burner fuels have a relatively narrow band of molecular sizes may require a more narrow slicing of the chromatogram in order to detect any effects, as recommended by Price [16].

A statistical analysis comparing aging in the thin film oven at various exposure times to aging in the plant or cores was not performed due to the small number of samples available. Plots of both physical measures and chromatograms shown in Chapter 6, however, indicate that the current standard of 5 hours exposure is not severe enough to approximate either plant aging or aging at 5 years of pavement life in Indiana. Further evaluation of

Table 8-6. Results of ANOVA on Detecting Changes in Asphalt

	Effects/Interaction						
Measure	S	P	F	S*P	S*F	F*P	S*F*P
PEN	+	-	-	-	+	-	-
KVIS	+	-	-	-	-	-	-
AVIS	+	-	-	-	-	-	-
PVN	+	-	-	-	-	-	-
VTS	+	-	+	-	-	-	-
AVISRAT	+	-	-	-	-	-	-
KVISRAT	+	-	-	-	-	-	-
PEN RET	+	-	+	-	+	-	-
LMS	-	-	-	-	-	+	-
MMS	+	-	-	-	-	-	-
SMS	+	-	-	-	-	-	-
Mw	+	+	-	-	+	-	-
Mn	+	-	+	-	-	+	-
POLY	+	-	-	-	-	-	-

Key: S = Stage Effects
P = Plant Effects
F = Fuel Effects
S*F = Interaction of Stage & Fuel
S*P = Interaction of Stage & Plant
F*P = Interaction of Fuel & Plant
\+ = Significant
\- = Not Significant

the TFOT exposure time using more samples and different asphalts should be considered.

8.3 - Discussion of Tests on Fuel Contamination

The results of tests on fuel contamination of the asphalt samples are presented in Chapter 7. Physical and chromatographic parameters of the contaminated and uncontaminated asphalts were measured, as well as strength measures of the mixes prepared with the uncontaminated and contaminated asphalts. All asphalt samples were contaminated with 1% burner fuel, as described in Chapter 4.

The analysis of variance (ANOVA) for the 1% contamination level was performed for both the physical measures and chromatographic parameters of the contaminated and uncontaminated asphalt. None of the measures of the physical parameters of the samples could detect differences between the contaminated and uncontaminated samples at the .05 level of significance. The physical parameters that were measured, their calculated F values and the p-values are shown in Table 8-7. These results confirm the lack of any consistency displayed in the graphs of the physical parameters of the samples shown in Chapter 7. A similar lack of capability to detect the effects of contamination was found in analysis of the physical measures of the uncontaminated and contaminated mixes. Marshall stability, Marshall flow and

Indirect Tensile strength measures all produced non significant values of F at the .05 level.

The chromatographic parameters of molecular size fractions (LMS, MMS, SMS) and the more commonly used molecular weight measures of Mw and Mn showed significant differences between contaminated and uncontaminated samples at the .05 level of significance. The results of this ANOVA are presented in Table 8-8 in the same format as the preceding table. The results of this analysis show significantly higher F statistics and lower p-values for the chromatographic parameters than did the statistical analysis of the physical parameters.

The analysis used to determine the effectiveness of physical measures of the asphalt, strength measures of the compacted mix and chromatographic measures of the asphalt to detect fuel contamination indicates that chromatographic measures can detect the differences between uncontaminated samples and samples contaminated with 1% burner fuel more effectively than can the physical measures of the asphalt cement or mix strength. None of the physical parameter or chromatographic measures, however, could be used to identify the three types of fuel used to contaminate the asphalt. The fact that different fuels could not be identified is due to the nature of the fuels. All three fuels studied are hydrocarbons exhibiting chromatograms with peaks at similar times of elution. At a level of contamination of only 1%, chromatographic analysis cannot

Table 8-7. Statistical Output for Physical Measures for Contamination

Physical Property	F-value	p-value	Significant?
Penetration	1.00	.9585	No
Kin. Viscosity	0.31	.5983	No
Abs. Viscosity	0.07	.8055	No
PVN	0.32	0.5928	No
VTS	0.95	0.3667	No

Table 8-8. Statistical Output for Chromatographic Measures for Contamination

Chromatographic Measure	F-value	p-value	Significant?
LMS	9.40	0.021	Yes
MMS	10.51	0.0177	Yes
SMS	9.62	0.0211	Yes
Mw	13.10	0.0111	Yes
Mn	7.37	0.0349	Yes
Polydispersity	2.59	0.1586	No
Mz	29.07	0.0017	Yes
Mz+1	39.31	0.0008	Yes

differentiate among the fuel types. Fuel differentiation is not as much a concern as is identification of its presence, however.

CHAPTER 9

SUMMARY AND CONCLUSIONS

This study used high pressure gel permeation chromatography (HPGPC) to evaluate asphalts used in Indiana during the 1985 paving season. The main objectives of this study were to: 1) develop HPGPC techniques to examine asphalts from different sources, 2) evaluate how the asphalt hot mix production process affects asphalts, and 3) determine to what extent incomplete combustion of burner fuels could be detected in asphalt mixes.

Tests were conducted on asphalts from sixteen different projects, representing samples produced in drum mix plants and those produced in batch plants. Two samples were selected for each type of burner fuel for each plant type. The same HPGPC system and procedures were used for preparation, injection and analysis for all samples. Summaries of the results and conclusions from the study are presented in the sections that follow.

9.1 - Tests of Original Asphalt Parameters

Samples of original asphalt were tested for their physical parameters and analyzed by HPGPC techniques. The results of both sets of tests were evaluated to determine whether correlations existed between physical parameters

and chromatographic parameters. An evaluation of the test results of this study led to the following conclusions:

1. The HPGPC techniques used in testing asphalt produce repeatable results when consistent preparation and testing procedures are used. These results did not identify changes for an asphalt obtained over a period of several weeks from one source.
2. Although some correlations could be established between physical parameters and chromatographic parameters for the asphalts studied, these correlations do not necessarily match correlations established by other researchers. This indicates that HPGPC analysis cannot be used reliably to predict asphalt parameters and performance for all asphalts. It is not possible at this point to conclude whether these differences are due to different asphalts or due to changes in specific equipment configuration.
3. HPGPC can be used to detect differences among different asphalts by comparing measures of the chromatograms.
4. Asphalt samples did not undergo measurable disassociation of agglomerated molecules in the carrier solvent when allowed to stand for several hours after the initial preparation.

9.2 - Tests on Changes in Asphalt with Aging

Samples of the sixteen asphalts were tested in the following stages: 1) original asphalt, 2) asphalt aged 5 hours in the thin film oven, 3) asphalt extracted from mix, and 4) asphalt extracted from cores after 5 years service life in a pavement. In addition to an evaluation of the changes in the asphalt due to aging, results were also analyzed to determine whether differences due to processing in different types of plants using different burner fuels could be detected. The conclusions that follow summarize these tests.

1. HPGPC analysis could detect differences in asphalts due to aging, but was not as sensitive as the evaluation of changes in physical parameters. HPGPC parameters that change significantly with aging are MMS, SMS, polydispersity and molecular weight.
2. The results of the study indicate that the LMS fraction of an asphalt does not change significantly with aging of the asphalt. This may indicate that the LMS fraction does not approximate the asphaltene fraction of an asphalt.
3. HPGPC analysis indicates that the results from the standard thin film oven test do not indicate as severe a change to asphalts as occurred in the asphalt plant or after 5 years

of service life for the asphalts studied.

4. Differences in asphalt due to hot mix asphalt production process and/or the burner fuel used in the drier could not be detected by either physical tests or HPGPC analysis.

9.3 - Tests on Fuel Contamination of Asphalt

Six samples representing the three different burner fuels which could contaminate the asphalt during processing in drum mix plants were tested in both the uncontaminated and contaminated conditions. A 1% contamination level was used to represent the level of contamination expected in an asphalt plant operating within emission guidelines. Based upon the evaluation of the changes in physical parameters of the asphalt, strength measures of the resulting mix, and HPGPC parameters, the following conclusions are presented:

1. HPGPC analysis could detect a 1% level of fuel contamination in the asphalt for #2 burner fuel, #4 burner fuel, and for reclaimed oil. This level of contamination could affect the physical properties or mix strength.

2. HPGPC analysis could not detect differences in the samples due to different burner fuels used to contaminate the asphalt.

3. An analysis of the conclusions from the three studies would indicate that the HPGPC analysis using the techniques in this research is best used as a comparative analysis tool to detect

changes in asphalt samples rather than to predict performance of an asphalt based upon chromatographic parameters. Changes due to different sources, stage of processing and fuel contamination can be detected by GPC if a baseline chromatogram of the asphalt is available for comparison with the tested sample.

CHAPTER 10

RECOMMENDATIONS FOR FURTHER STUDY

The results of this study and the research work performed by earlier researchers indicate that high pressure-gel permeation chromatography techniques have significant applications for the analysis of asphalt. Some of the areas with potential for further study, and equipment/procedural change recommendations are presented in the two sections that follow in this chapter.

10.1 Research Activities

Areas for further research potential are as follows:

1. Samples should be analyzed with varying amounts of asphaltene fractions added into samples in order to evaluate the correlation between asphaltene content and age hardening properties. Samples should be separated into fractions with appropriate solvents, and introduced back into asphalt samples in increasing amounts. HPGPC analysis should show changes in the size fractions with increases in the fractions.
2. A more detailed study of thin film oven testing (TFOT) effects on asphalt would be helpful in

identifying the level of age hardening simulated by oven tests. TFOT exposed samples of varying ages can be compared to asphalt samples of various ages and to Rolling Thin Film Oven samples of comparable ages. Chromatographic analysis will also be useful in performing an evaluation of the changes in Large Molecular Size fractions in the asphalts following exposure.

3. Further studies of the effects of type of hot mix asphaltic concrete production plants on age hardening of the asphalt cement should be performed.

4. The asphalt samples collected during the 1985 paving season should be tested in the future, in order to determine long-term effects of age hardening. Possibly, seven or ten year testing of the asphalt samples could be performed and compared to cores taken at those times.

10.2 Equipment/Procedure Changes

The HPG-PC system and data analysis software used in this study represented the best of what is readily available to the asphalt researcher today and are a major improvement over systems available to earlier researchers. Some further recommendations for improvements to the system and the procedures used in this study follow.

1. The system pump has a tendency to foul (clog) when shut down for extended periods of time. This problem may be alleviated by allowing the system to keep running at a low flow rate (0.30 ml/min) when not testing. In order to conserve solvent, the return line may discharge into the solvent bottle, producing a closed flow system.
2. The Waters Model 590 pump produces a vibration at 1.00 ml/min. This vibration can be reduced by maintaining the flow at 0.950 or 1.050 ml/min.
3. Screen resolution of chromatograms is excellent with the 820 software, but a high density printer or compatible plotter is required in order to transfer results to paper adequately.
4. A tape storage system should be utilized to save chromatograms for future evaluation, especially if seven or ten year studies are undertaken. The hard drive currently being used (20 megabyte), is over ninety percent full with the 820 system software and stored chromatographic data.

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